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Perturbation Theories of Weak Intermolecular Forces

by

Phillip Robinson Certain

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by

Phillip Robinson Certain

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requirements for the degree of

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ERRATA

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PERTURBATION THEORIES OF WEAK INTERMOLECULAR FORCES^{*}

Phillip Robinson Certain

Under the supervision of Professor Joseph O. Hirschfelder

ABSTRACT

This thesis is a contribution to the development of a workable exchange perturbation theory for intermolecular forces. It is divided into three parts. The first part develops a perturbation formalism for degenerate and almost degenerate energy states. The formalism is related to methods of Van Vleck, Kato, Bloch, Hirschfelder, Kirtman, and Löwdin and can have a greater range of validity than the Rayleigh-Schrödinger perturbation theory. The second part extends the formalism to exchange problems and leads to the Hirschfelder-Silbey perturbation theory. A method of solving the first order equation is developed which reduces the many electron equation to one and two electron equations. The third part applies four different perturbation formalisms for exchange forces to three model problems: the hydrogen molecule at internuclear separations $R = 4, 6, 8 a_0$; a harmonic oscillator model of the hydrogen molecule ion; and the delta-function model of the hydrogen molecule ion.

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FOREWORD

This thesis is a contribution to the development of a workable "exchange" perturbation theory for intermolecular forces, which starts from the isolated molecules as the unperturbed state, but which takes account of the full symmetry of the interacting system, including the Pauli exclusion principle.

In Chapter One the mathematical difficulties associated with exchange perturbation theory are discussed, and it is shown that many different expansions of the wavefunction are possible. A brief historical survey of the formalisms which have been proposed is given.

In preparation for exchange perturbation theory, a perturbation formalism for degenerate and almost degenerate energy states is developed in Chapter Two. The formalism is related to methods of Van Vleck, Kato, Bloch, Hirschfelder, Kirtman, and Lowdin. It has the feature of giving the energy as the root of a secular equation. The matrix elements of the secular equation are assumed to be analytic in the perturbation parameter, but not necessarily the energy. Thus, the treatment can have a greater range of validity than the Rayleigh-Schrödinger perturbation theory. The connection of the formalism with Lowdin's partitioning technique is investigated. It is shown that if the two methods are truncated at the same order, they give the same results for the energy and wavefunction, except for higher order terms.

In Chapter Three the extension of the formalism of Chapter Two to exchange problems is shown to be equivalent to the Hirschfelder-Silbey perturbation theory. It is also shown that the first order perturbation equation can be separated into a polarization equation,

which introduces van der Waals correlations, and an exchange equation, which introduces ionic terms. In the many electron case, these equations can be reduced to one and two electron equations.

In addition to the Hirschfelder-Silbey (HS) procedure, exchange perturbation formalisms have been proposed by Eisenschitz and London, van der Avoird, and Hirschfelder (EL-HAV); Muirrell and Shaw, and Musher and Amos (MS-MA); and others. A Sternheimer (RS) expansion is also possible for one and two electron problems. Assuming convergence, each perturbation expansion yields the exact energy and wavefunction if carried to infinite order. In any practical application, however, the energy is computed to low order only, and at this level of approximation, the different approaches give different results. It then becomes of interest to ask the question: "Which formalism provides the best second order energy and the best expectation value of the hamiltonian using the wavefunction accurate through first order?"

In Chapter Four an attempt is made to answer this question on the basis of model calculations. The energies of both the ground state ($^1\Sigma_g^+$) and the first excited state ($^3\Sigma_u^+$) of the hydrogen molecule are computed at internuclear separations $R = 4, 6, 8a_0$, using the EL-HAV, MS-MA, HS, and RS formalisms. The results, discussed in detail in Chapter Four, do not show that any of the schemes is outstandingly better than the other three. The second order energy in the EL-HAV expansion, however, appears to approach one-half of the second order polarization (dispersion) energy at large values of R . The other formalisms give good values for the energy in the region of the van der Waals minimum for the $^3\Sigma_u^+$ state, although at shorter distances

the error increases. Also considered are a harmonic oscillator model and the double minimum delta-function model of the H_2^+ problem. These calculations verify the long-range behavior of the EL-HAV second order energy.

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I. INTRODUCTION

The study of intermolecular forces is essential to the understanding of most of the physical properties of matter, such as equations of state, transport properties, scattering cross-sections, and so on. For intermolecular forces¹ govern all of the attractive and repulsive interactions between atoms and molecules, as opposed to chemical forces, which hold a single molecule together and prevent it from separating into its constituent atoms. Of course, there is no precise difference between these two kinds of force, except in orders of magnitude. According to Pauling,²

there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species.

Intermolecular forces, on the other hand, are sufficiently weak so that any aggregates that are formed, are transitory in nature and easily destroyed by thermal motion. It is best, however, not to emphasize the difference between intermolecular and chemical forces too much.

Quantum mechanical perturbation theory has long been used to systemize the study of intermolecular forces.³ Although it is convenient to speak of forces, a more basic theoretical quantity is the electronic interaction energy, $(E - E^{(0)})$. (The Born-Oppenheimer separation⁴ of the nuclear and electronic motions is assumed throughout this thesis, and relativistic effects are neglected.) The force.

on a particular molecule is the negative gradient of the interaction energy with respect to the nuclear coordinates of the molecule.

The electronic energy E is obtained as an eigenvalue of the Schrödinger equation

$$(H - E) \Psi = 0, \quad (1.1)$$

where the total hamiltonian H is a sum of $H^{(0)}$, the electronic hamiltonian for the isolated molecules (i.e. separated from each other by infinite distances), and $H^{(1)}$, the sum of all of the coulombic interactions between electrons and nuclei belonging to different molecules. The energy $\epsilon^{(0)}$ is the electronic energy of the isolated molecules and is an eigenvalue of the Schrödinger equation

$$(H^{(0)} - \epsilon^{(0)}) \phi^{(0)} = 0, \quad (1.2)$$

where $\phi^{(0)}$ is a simple product of isolated molecule wavefunctions.

The simplest application of perturbation theory to the calculation of $(E - \epsilon^{(0)})$ is the polarization expansion,⁵ which is a straightforward application of Rayleigh-Schrödinger perturbation theory. The unperturbed problem is Eq. (1.2), and the theory leads to an expansion of the interaction energy in powers of the perturbation $H^{(1)} = H - H^{(0)}$. If the terms are further expanded in inverse powers of the separations between the molecules, each term may be given a classical or quasi-classical interpretation as arising from interactions between either permanent or instantaneous multipole moments of the separated molecules. In this way are identified electrostatic forces, due to the

permanent moments of the molecules; induction forces, due to the permanent moment of one molecule inducing a moment in the other; dispersion forces, due to the instantaneous moments of the molecules; and resonance forces, which can arise if the level $\epsilon^{(0)}$ is degenerate, and which behave as electrostatic forces. Such a classification is of unquestioned utility in understanding a wide variety of experimental results on a qualitative basis, and in providing a starting point for semi-empirical theories.⁶

The polarization expansion is applicable only when the molecules are well separated, however, and does not predict chemical binding between molecules. As Heitler and London⁷ showed, binding is obtained with an approximate wavefunction which is an antisymmetrized product of isolated molecule functions, and which satisfies the Pauli exclusion principle; i.e., which changes sign upon the exchange of any two electron labels. The added terms in the expression for $(E - \epsilon^{(0)})$ are called exchange forces; from the standpoint of perturbation theory, such terms result from a first order treatment.

Mathematical Complications. Difficulties arise when perturbation theory is applied to the accurate, ab initio determination of intermolecular forces in case that it is necessary to go beyond first order and also to take explicit account of the exclusion principle. At internuclear separations short enough so that the electronic clouds of the molecules overlap, the total wavefunction Ψ is required to have symmetry properties corresponding to the total hamiltonian H , which is symmetric with respect to the exchange of any pair of electrons between the two molecules. The most natural choice for the unperturbed

hamiltonian, $H^{(0)}$, is the sum of the hamiltonians for the non-interacting molecules. However, this implies associating particular electrons with definite molecules. Hence the symmetry of H with respect to electron permutations is greater than that of $H^{(0)}$. The difficulties to which this gives rise are known as the exchange problem.

Another basic difficulty is that the order of the perturbation terms is not uniquely defined. If A is the operator which projects the component with the symmetry of the desired total wavefunction, then A commutes with H . However, A does not commute separately with either $H^{(0)}$ or the perturbation $H^{(1)}$, but rather,

$$[A, H^{(0)}] = [H^{(1)}, A] \quad (1.3)$$

In any conventional perturbation scheme, the left hand side of Eq. (1.3) is zeroth order and the right hand side is first order. This equation means that "order in $H^{(1)}$ " is not a well defined concept, and that the apparent order of various terms in a perturbation expansion can be arbitrarily shifted.

Related to the nonuniqueness of order is the difficulty of defining a symmetrized basis set for the expansion of Ψ . A natural choice consists of the set $A\phi_k^{(0)}$, where the $\phi_k^{(0)}$ are the complete set of eigenfunctions of $H^{(0)}$,

$$(H^{(0)} - \epsilon_k^{(0)})\phi_k^{(0)} = 0, \quad (1.4)$$

where $H^{(0)}$ is the isolated molecule hamiltonian and $\phi_k^{(0)}$ is a simple product of isolated molecule wavefunctions. The basis $A\phi_k^{(0)}$ is

nonorthogonal, however, whereas nondegenerate eigenfunctions of a hermitean hamiltonian are necessarily orthogonal. Thus it is impossible to define a single, hermitean unperturbed hamiltonian, of which every $A\phi_k^{(\omega)}$ is an eigenfunction. In particular, since $H^{(\omega)}$ and A fail to commute, the $A\phi_k^{(\omega)}$ are not eigenfunctions of $H^{(\omega)}$.

Another lack of uniqueness is due to the fact that the complete set of symmetrized functions $A\phi_k^{(\omega)}$ are linearly dependent. To prove this, consider a function Ω which has symmetry different from A , i.e. $A\Omega = 0$. Since the $\phi_k^{(\omega)}$ are complete, Ω has the unique expansion

$$\Omega = \sum_k \phi_k^{(\omega)} c_k, \quad (1.5)$$

where the c_k are constants. By hypothesis, $A\Omega$ vanishes, so that

$$A\Omega = 0 = \sum_k A\phi_k^{(\omega)} c_k, \quad (1.6)$$

which is a statement of linear dependence of the set $A\phi_k^{(\omega)}$. For a simple example of Eq. (1.5) and (1.6), consider the interval $-1 \leq x \leq 1$ and let A project the symmetric component of any function $f(x)$:

$Af(x) = \frac{1}{2}f(x) + \frac{1}{2}f(-x)$. A complete set of unsymmetric functions on this interval is $\phi_k^{(\omega)} = (x - \frac{1}{2})^k$, so that $c_k = \frac{1}{k!} \left[\frac{d^k \Omega}{dx^k} \right]_{x=\frac{1}{2}}$. If $\Omega = x^3$, then $\Omega = \phi_3^{(\omega)} + \frac{3}{2}\phi_2^{(\omega)} + \frac{3}{4}\phi_1^{(\omega)} + \frac{1}{8}\phi_0^{(\omega)}$

and $Ax^3 = 0 = A\phi_3^{(\omega)} + \frac{3}{2}A\phi_2^{(\omega)} + \frac{3}{4}A\phi_1^{(\omega)} + \frac{1}{8}A\phi_0^{(\omega)}$.

Moreover, the linear dependence of the $A\phi_k^{(\omega)}$ is non-trivial in case that it is possible to find a function Ω such that $A\Omega = 0$

and each c_k in Eq. (1.5) is nonvanishing. (In the previous example put $\Omega = \sin \pi X/2$). Then it follows that it is impossible to construct a linearly independent set by excluding a finite number of $A\phi_k^{(o)}$ from the original set. For example, $A\phi_1^{(o)}$ can be eliminated from Eq. (1.6) by the expansion

$$A\phi_1^{(o)} = \sum_k \phi_k^{(o)} a_k = \sum_k A\phi_k^{(o)} a_k,$$

or

$$A\phi_1^{(o)} = \sum_{k \neq 1} A\phi_k^{(o)} \left[\frac{a_k}{1-a_1} \right]. \quad (1.7)$$

Substituting Eq. (1.7) into Eq. (1.6) yields

$$0 = \sum_{k \neq 1} A\phi_k^{(o)} \left[c_k + \frac{c_1 a_k}{1-a_1} \right].$$

Thus the set $A\phi_k^{(o)}$, $k \neq 1$, is also linearly dependent.

This means that no unique expansion of the total wavefunction of the form

$$\Psi = \sum_k A\phi_k^{(o)} c_k \quad (1.8)$$

is possible.

The above considerations do not imply that it is impossible to develop a perturbation expansion for intermolecular forces that takes full account of symmetry, but rather that many different approaches are possible.

Historical Survey of Exchange Perturbation Theories. The oldest perturbation theory which takes the exclusion principle into account was developed by Eisenschitz and London.⁸ The formalism was recently put into a more modern notation by van der Avoird.⁹ These authors assumed the expansion Eq. (1.8). Of course, they recognized the lack of uniqueness of such an expansion, but nevertheless resolved the Schrödinger equation into an infinite set of perturbation equations which can be solved in a well defined, though arbitrary, way. Their expression for the first order interaction energy agrees with the Heitler-London result. The second order energy is expressed in a sum over states form, which when evaluated by the Unsöld method¹⁰ gives the second order polarization energies, modified by the effects of exchange.

Dalgarno and Lynn¹¹ have introduced the Unsöld approximation to the second order energy of a Brillouin-Wigner expansion and obtained the same result as Eisenschitz and London.

Van der Avoird¹² has recently given an elegant wave operator formalism which gives the same expression for the first and second order energy as the Eisenschitz-London expansion. Hirschfelder¹³ has also derived van der Avoird's equations without the introduction of the wave operators.

Musher and Salem¹⁴ have also assumed the expansion of Ψ given by Eq. (1.8). These authors used a Feenberg¹⁵ iteration technique to evaluate the coefficients, however, and obtained a different expression for the second order energy. This approach has the feature of not requiring H to be separated into $H^{(0)} + H^{(1)}$

Other examples in which the expansion Eq. (1.8) is used is the work of Murrell, Randić and Williams¹⁶ and of Salem.¹⁷ The former authors assumed that Eq. (1.8) consists of a finite number of terms which includes both covalent and ionic type functions. This allows questions of over-completeness to be avoided, and is equivalent to solving a finite dimensional secular equation by a perturbation expansion. Salem makes the assumption that $\langle A\phi_k^{(o)} | A\phi_l^{(o)} \rangle = \delta_{kl}$, which does not hold for the functions defined by Eq. (1.4), but which is useful in assessing the significance of various terms in Eq. (1.8).

A different type of expansion of Ψ was assumed by Murrell and Shaw,¹⁸ who used a wave operator approach, and in an equivalent¹⁹ treatment by Musher and Amos,²⁰ who started from an infinite secular equation. These authors assumed that the zeroth order component of Ψ has proper symmetry, but that the remainder can be expanded in the unsymmetrized functions $\phi_k^{(o)}$. Hence

$$\Psi = A\phi^{(o)} + \sum_k' \phi_k^{(o)} c_k$$

The expansion in this set of functions is unique, although the higher order terms do not have definite symmetry properties, order by order.

A different class of approaches to the exchange problem involves different ways of defining and computing a "primitive function" whose projection onto the space of desired symmetry is the total wavefunction Ψ , in the same sense that the zeroth order function $A\phi^{(o)}$ is the projection of $\phi^{(o)}$. Hirschfelder and Silbey²¹ propose that there is a physically significant primitive function whose symmetry

projections correspond to all the wave functions for the family of states arising from a single electron configuration. Related approaches have been discussed by Herring,²² Musher and Silbey,²³ and Kirtman.²⁴

Jansen²⁵ (see also Byers Brown²⁶ and Ritchie²⁷) has explicitly constructed an operator Λ which operates on a symmetrized function $A\Omega$ to produce a function in which specific electrons are assigned to particular atoms. With Λ he is able to construct an unperturbed "label free" hamiltonian whose eigenfunctions are $A\phi_R^{(0)}$.

Corinaldesi²⁸ replaced the Schrödinger equation by a "modified Schrödinger equation" in which the wavefunction is represented by a vector, each component of which represents a different assignment of electrons to molecules. The modified equation is then solved by a perturbation expansion and the true wavefunction is obtained as a linear combination of the vector components.

Applications of Exchange Perturbation Theories. Numerical applications of some of the formalisms have been reported previously. In their original paper Eissenschitz and London⁸ considered the interaction of ground state hydrogen atoms. More recently, the hydrogen molecule has been considered by Alexander and Salem,²⁹ who used the formalism of Musher and Salem,¹⁴ and by Corinaldesi.²⁸ Jansen and coworkers³⁰ have applied his theory to the calculation of a wide range of crystal properties. Van der Avoird³¹ has treated adsorption on metal surfaces by his method. Murrell and Shaw³² have computed the interaction energy of two helium atoms; and Duijneveldt and Murrell³³ have treated problems involving hydrogen bonding.

In all of these treatments, however, approximations have been made to various terms in the perturbation expansions, thus obscuring the efficacy of the exact perturbation series. Also, for most of the applications the exact answer to the problem is unknown, so that it is difficult to judge the convergence properties of the expansions. Exceptions to this are the calculation of van der Avoird³¹ of the H_2^+ potential, the solution of a spin model by Johnson and Epstein,³⁴ and the application of the Hirschfelder-Silbey procedure²¹ to H_2^+ by McQuarrie and Hirschfelder.³⁵

II. PERTURBATION THEORY FOR DEGENERATE AND ALMOST DEGENERATE STATES

In this Chapter, a formalism is developed for treating the effect of a perturbation upon a set of degenerate energy states of an unperturbed hamiltonian. The formalism, which is related to methods of Van Vleck,³⁶ Kato,³⁷ Bloch,³⁸ Hirschfelder,³⁹ Kirtman,⁴⁰ and Lowdin,⁶⁵ has the feature of giving the energy as the root of a secular equation. The matrix elements of the secular equation are assumed to be analytic in the perturbation parameter, but not necessarily the energy. Thus the treatment can have a greater range of validity than the Rayleigh-Schrödinger perturbation theory. If the formalism of this Chapter is expanded in powers of the perturbation parameter, however, the usual Rayleigh-Schrödinger theory is obtained. The connection of the formalism with the partitioning technique⁶⁵ is established in Appendix C.

2.1 Brief Review of Rayleigh-Schrödinger Perturbation Theory.

Consider the solution of the Schrödinger equation

$$(H(\lambda) - E_q(\lambda)) \Psi_q(\lambda) = 0, \quad (2.1)$$

where the hamiltonian is the sum of two terms,

$$H(\lambda) = H^{(0)} + \lambda H^{(1)} \quad (2.2)$$

The $H^{(0)}$ is the hamiltonian for the unperturbed system, and the $H^{(1)}$ is a perturbation. The parameter λ in some cases has physical significance (e.g. field strength), but otherwise is a formal ordering parameter with physical value of unity.

The unperturbed hamiltonian is assumed to possess a complete set of eigensolutions,

$$(H^{(0)} - E_q^{(0)}) \psi_q^{(0)} = 0.$$

The perturbed wavefunctions Ψ_q can be expanded in the set $\psi_p^{(0)}$,

$$\Psi_q = \sum_p \psi_p^{(0)} b_{pq}(\lambda),$$

where $b_{pq}(\lambda=0) = \delta_{pq}$.

The fundamental assumption of Rayleigh-Schrödinger perturbation theory is that both Ψ_q and E_q are analytic functions of the parameter λ ; hence,

$$E_q(\lambda) = E_q^{(0)} + \sum_{n=1}^{\infty} \lambda^n E_q^{(n)}, \quad (2.3)$$

$$b_{pq}(\lambda) = \delta_{pq} + \sum_{n=1}^{\infty} \lambda^n b_{pq}^{(n)},$$

and

$$\Psi_q(\lambda) = \psi_q^{(0)} + \sum_{n=1}^{\infty} \lambda^n \psi_q^{(n)}, \quad (2.4)$$

where

$$\psi_q^{(n)} = \sum_p \psi_p^{(0)} b_{pq}^{(n)}$$

Substituting the expansions (2.2), (2.3), and (2.4) into (2.1), and setting the coefficient of each power of λ to zero yields an infinite set of inhomogeneous equations for the $\psi_q^{(n)}$ and $E_q^{(n)}$:

$$(H^{(0)} - E_q^{(0)}) \psi_q^{(n)} + (H^{(1)} - E_q^{(1)}) \psi_q^{(n-1)} = \sum_{m=0}^{n-2} E_q^{(n-m)} \psi_q^{(m)}. \quad (2.5)$$

For $n = 1$, the upper limit of the sum in Eq. (2.5) is greater than the lower limit. The convention adopted in this thesis is that when this occurs, the sum vanishes.

The perturbation energies are determined by multiplying Eq. (2.5) from the left by $\psi_q^{(0)*}$ and integrating. Then by a series of algebraic manipulations involving the perturbation Eqs. (2.5), it is possible to show⁴¹ that

$$\begin{aligned} E_q^{(2n)} = & \langle \psi_q^{(n-1)} | H^{(1)} | \psi_q^{(n)} \rangle - \sum_{k=1}^n E_q^{(k)} \sum_{j=0}^{k-1} \langle \psi_q^{(n+j-k)} | \psi_q^{(n-j)} \rangle \\ & - \sum_{k=1}^{n-1} E_q^{(2n-k)} \sum_{j=0}^k \langle \psi_q^{(j)} | \psi_q^{(k-j)} \rangle ; \end{aligned} \quad (2.6)$$

$$\begin{aligned} E_q^{(2n+1)} = & \langle \psi_q^{(n)} | H^{(1)} | \psi_q^{(n)} \rangle - \sum_{k=1}^n E_q^{(k)} \sum_{j=0}^{k-1} \langle \psi_q^{(n+1+j-k)} | \psi_q^{(n-j)} \rangle \\ & - \sum_{k=1}^n E_q^{(2n+1-k)} \sum_{j=0}^k \langle \psi_q^{(j)} | \psi_q^{(k-j)} \rangle . \end{aligned} \quad (2.7)$$

Eqs. (2.6) and (2.7) are completely general regardless of the degeneracy and the normalization of the wavefunction. These equations demonstrate the Wigner theorem that a knowledge of the wavefunction accurate through $\mathcal{O}(\lambda^n)$ is sufficient to determine the energy through $\mathcal{O}(\lambda^{2n+1})$.

Normalization conditions are required to complete the specification of the perturbed functions. There are two types of normalization in common use. For full normalization, the exact wavefunction Ψ_q is required to be normalized to unity. Substituting the expansion (2.4) into $\langle \Psi_q | \Psi_q \rangle = 1$ yields

$$\sum_{k=0}^n \langle \psi_q^{(n-k)} | \psi_q^{(k)} \rangle = 0, \quad n \geq 1. \quad (2.8)$$

For intermediate normalization, the requirement is that

$$\langle \psi_q^{(\omega)} | \Psi_q \rangle = \langle \psi_q^{(\omega)} | \psi_q^{(\omega)} \rangle = 1, \text{ or, expanding in powers of } \lambda,$$

$$\langle \psi_q^{(\omega)} | \psi_q^{(n)} \rangle = 0, \quad n \geq 1.$$

In practice the series (2.3) and (2.4) are computed up to some finite order only. It is convenient to define the partial sums

$$\Psi_q(N) = \sum_{n=0}^N \lambda^n \psi_q^{(n)}, \quad (2.9)$$

and

$$E_q(N) = \sum_{n=0}^N \lambda^n E_q^{(n)}.$$

The radius of convergence of the expansions (2.3) and (2.4) is, in general, difficult to ascertain. In many cases the $E_q^{(n)}$ and $b_{pq}^{(n)}$ are finite for all n , even though the expansions do not converge for required values of λ . Then it can be shown⁴² that the perturbation series is an asymptotic expansion of both the energy and the wavefunction. Since the error in truncating an asymptotic expansion is of the order of magnitude of the last term retained, the

expansions (2.3) and (2.4) are expected to provide good approximations to the true energy and wavefunction of a state q if the quantities $b_{pq}^{(n)}$ are small. For $n = 1$, the solution of Eq. (2.5) gives

$$b_{pq}^{(1)} = \frac{\langle \psi_p^{(0)} | H^{(1)} | \psi_q^{(0)} \rangle}{\epsilon_q^{(0)} - \epsilon_p^{(0)}} , \quad (2.10)$$

so that a rough criterion for accuracy is

$$|\langle \psi_p^{(0)} | H^{(1)} | \psi_q^{(0)} \rangle| \ll |\epsilon_p^{(0)} - \epsilon_q^{(0)}|. \quad (2.11)$$

When the states p and q are degenerate or almost degenerate, the right hand side of the inequality (2.11) is small, whereas the left side can be large, so that the expansions (2.3) and (2.4) become unreliable. If the closely spaced levels are well separated from the remaining states, however, it is possible to modify the Rayleigh-Schrödinger treatment to avoid the expansion of $b_{pq}(\lambda)$ if p and q are degenerate or almost degenerate, while retaining the expansion for widely separated levels. This modification is developed in the next Section. An alternative approach, the partitioning technique,⁶⁵ is discussed in Appendix C.

2.2 General Formulation.

Consider the linear manifold \mathcal{S} which is spanned by S' eigenfunctions Ψ_k , $1 \leq k \leq S'$, of the total Schrödinger equation (2.1). \mathcal{S} is defined to have the property that if state k in \mathcal{S} has the zeroth order energy $\epsilon_k^{(0)}$, then all states k' which have zeroth

order energies $\epsilon_k^{(0)}$ that are degenerate or almost degenerate with $\epsilon_k^{(0)}$, are in \mathcal{S} . The sequential labelling of the states by k is for convenience and does not imply that they are the S lowest energy states of H .

The Ψ_k constitute an orthonormal basis for manifold \mathcal{S} . Any other basis in \mathcal{S} may be defined by

$$\Phi_k = \sum_{\ell=1}^S \Psi_{\ell} C_{\ell k}, \quad (2.12)$$

where the numbers $C_{\ell k}$ are elements of a non-singular transformation. The basic idea in introducing the Φ_k is to choose the coefficients $C_{\ell k}$ in such a way that, when $\Phi_k(\lambda)$ is expanded into powers of λ analogous to Eq. (2.4), such terms as Eq. (2.10), with p and q both belonging to \mathcal{S} , do not occur. Thus the expansion of Φ_k in powers of λ , can be expected to have a greater range of validity than the expansion of Ψ_k .

The basis functions Φ_k satisfy the coupled equations

$$H \Phi_k = \sum_{\ell=1}^S E_{\ell} \Psi_{\ell} C_{\ell k} = \sum_{j=1}^S \Phi_j \epsilon_{jk}, \quad (2.13)$$

where

$$\epsilon_{jk} = \sum_{\ell=1}^S C_{j\ell}^{-1} E_{\ell} C_{\ell k},$$

and

$$\delta_{jk} = \sum_{\ell=1}^S C_{j\ell}^{-1} C_{\ell k}. \quad (2.14)$$

Given the basis functions Φ_k , the eigensolutions (E_k, Ψ_k) are recovered by solving the secular equation

$$|\langle \Phi_k | H - E | \Phi_\ell \rangle| = 0. \quad (2.15)$$

Thus, Eq. (2.13) and (2.15) are equivalent to the S uncoupled Schrödinger equations for (E_k, Φ_k) . Although Φ_k and $\epsilon_{k\ell}$ will later be expanded in powers of λ , it is not assumed that the roots of Eq. (2.15) are analytic in λ . This is, it is assumed that the matrix elements of H are analytic, but not necessarily the energy eigenvalues. An example where such an assumption is valid occurs for the interaction of two $2s$ or $2p$ hydrogen atoms, as discussed by Kim and Hirschfelder.⁵⁹ See also the example in Section 2.5.

At this point it is convenient to introduce a more compact notation. Matrices will be denoted by "fat" symbols; e.g.,

$$\mathbb{E} = (\epsilon_{k\ell}),$$

$$\Phi = (\Phi_k) = (\Phi_1, \Phi_2, \dots, \Phi_s)$$

See Appendix A for a full explanation of the notation. In this notation, Eq. (2.13) and (2.15) become

$$H\Phi = \mathbb{E}\Phi \quad (2.13)$$

and

$$|\langle \Phi | H - E | \Phi \rangle| = 0 \quad (2.15)$$

Alternative Derivation of Equation (2.13). In order to clarify the meaning of Eq. (2.13) it is useful to give another derivation, based on Kirtman's treatment⁴⁰ of Van Vleck degenerate perturbation theory.³⁶

Consider a complete set of functions, which is split into two classes, $\phi^{(0)}$ and $\chi^{(0)}$, and which spans the Hilbert space of the hamiltonian $H(\lambda) = H^{(0)} + \lambda H^{(1)}$. One class, to which special attention is given, consists of the finite set of S functions,

$$\phi^{(0)} = (\phi_1^{(0)}, \phi_2^{(0)}, \dots, \phi_S^{(0)})$$

Each $\phi_k^{(0)}$ is assumed to be an eigenfunction of the unperturbed hamiltonian $H^{(0)}$,

$$(H^{(0)} - \epsilon_k^{(0)}) \phi_k^{(0)} = 0, \quad 1 \leq k \leq S.$$

If the eigenvalue $\epsilon_k^{(0)}$ is degenerate, then it is assumed that all of the corresponding eigenfunctions are included in $\phi^{(0)}$. Further, it is assumed that the $\phi_k^{(0)}$ are orthonormal,

$$\langle \phi^{(0)} | \phi^{(0)} \rangle = 1,$$

where 1 is the unit matrix.

The remaining functions (in general, infinite in number) which complete the set are denoted by

$$\chi^{(0)} = (\chi_1^{(0)}, \chi_2^{(0)}, \dots).$$

Without loss of generality, it is assumed that

$$\langle \chi^{(0)} | \chi^{(0)} \rangle = 1$$

and

$$\langle \chi^{(0)} | \phi^{(0)} \rangle = 0,$$

where 0 is the null matrix. No other assumptions are made regarding $\chi^{(0)}$; in particular, the $\chi_k^{(0)}$ is not necessarily an eigenfunction of $H^{(0)}$.

The set $\phi^{(0)}$ is a basis of unperturbed functions for the approximate calculation of S eigenstates $(E_k(\lambda), \Psi_k(\lambda))$ of the total hamiltonian $H(\lambda)$, where

$$E_k(\lambda=0) = \epsilon_k^{(0)} \quad 1 \leq k \leq S$$

In general, to complete the (E_k, Ψ_k) exactly, it is necessary to consider both $\phi^{(0)}$ and $\chi^{(0)}$ since the interaction elements $\langle \phi^{(0)} | H | \chi^{(0)} \rangle$ are non-vanishing. Then the E_k are roots of the infinite-dimensional secular equation

$$\begin{vmatrix} \langle \phi^{(0)} | H-E | \phi^{(0)} \rangle & \langle \phi^{(0)} | H-E | \chi^{(0)} \rangle \\ \langle \chi^{(0)} | H-E | \phi^{(0)} \rangle & \langle \chi^{(0)} | H-E | \chi^{(0)} \rangle \end{vmatrix} = 0. \quad (2.16)$$

Following Van Vleck³⁶ and Kirtman,⁴⁰ the solution of Eq. (2.16) is obtained by transforming the initial basis into the new set

$$\Phi(N) = \phi^{(0)} + \lambda \phi^{(1)} + \dots + \lambda^N \phi^{(N)},$$

and

$$\chi(N) = \chi^{(0)} + \lambda \chi^{(1)} + \dots + \lambda^N \chi^{(N)}.$$

The functions $\phi^{(k)}$, $\chi^{(k)}$ are chosen so as to make the overlap and hamiltonian matrix elements connecting $\Phi(N)$ and $\chi(N)$ vanish through terms $O(\lambda^N)$:

$$\langle \Phi(N) | H - E | \Phi(N) \rangle = O(\lambda^{N+1}).$$

Then the leading contribution of the functions $\chi^{(N)}$ to the energies E_k , $1 \leq k \leq S$, is proportional to

$$|\langle \Phi(N) | H | \chi(N) \rangle|^2 = O(\lambda^{2N+2})$$

Hence the roots of the $S \times S'$ secular equation,

$$|\langle \Phi(N) | H - E | \Phi(N) \rangle| = 0, \quad (2.17)$$

are accurate through $O(\lambda^{2N+2})$.

To obtain equations for $\phi^{(k)}$, $\chi^{(k)}$, it is convenient to introduce the projector onto the set $\Phi(N)$:

$$\mathcal{O} = \mathcal{O}^\dagger = \mathcal{O}^2;$$

$$\mathcal{O} \Phi(N) = \Phi(N).$$

The perturbation terms of $\chi(N)$ are given by

$$\chi(N) = (1 - \mathcal{O}) \chi^{(0)},$$

which assures orthogonality between $\Phi(N)$ and $\chi(N)$ through $\mathcal{O}(\lambda^N)$.

The perturbation terms of $\Phi(N)$ are determined by

$$|\langle \Phi(N) | H | \chi(N) \rangle| = \mathcal{O}(\lambda^{N+1}). \quad (2.18)$$

The $\chi(N)$ is a complete set of functions in the space orthogonal to

$\Phi(N)$. If overlap of $H\Phi(N)$ with all of $\chi(N)$ vanishes, then

$H\Phi(N)$ must be expressible as a linear combination of the $\Phi(N)$.

Thus, Eq. (2.18) is equivalent to

$$H\Phi(N) = \Phi(N) \mathcal{E}(N) + \mathcal{O}(\lambda^{N+1}) \quad (2.19)$$

where the elements of $\mathcal{E}(N)$ are numbers to be determined. In the

limit $N \rightarrow \infty$, Eq. (2.19) clearly becomes Eq. (2.13).

Perturbation Expansion. Viewed as equations for the Φ_k and

\mathcal{E}_{lk} , Eqs. (2.13) and (2.15) are not well-defined, however, since

all reference to the particular linear manifold \mathcal{L} has been lost.

That is, Eq. (2.13) has solutions in any S-dimensional linear manifold

defined by the exact eigenfunctions of H . Furthermore, within any

particular linear manifold, there is an infinite number of solutions

of Eq. (2.13) corresponding to different choices for the coefficients

\mathcal{C}_{lk}

The lack of uniqueness in Eq. (2.13) is obviated by a perturbation approach to its solution. The following expansions are assumed:

$$\begin{aligned} H &= H^{(0)} + \lambda H^{(1)}, \\ \Phi &= \sum_{n=0}^{\infty} \lambda^n \Phi^{(n)}, \\ \mathcal{E} &= \sum_{n=0}^{\infty} \lambda^n \mathcal{E}^{(n)} \end{aligned} \quad (2.20)$$

The linear manifold \mathcal{L} is uniquely determined by specifying the zeroth order energies

$$\mathcal{E}_n^{(0)} = \mathcal{E}_k^{(0)} \delta_{kl} \quad (2.21)$$

Substituting the expansions (2.20) into (2.13) and setting the coefficient of each power of λ equal to zero yields the infinite set of equations

$$H \Phi^{(0)} = \Phi^{(0)} \mathcal{E}^{(0)},$$

and

$$H^{(0)} \Phi^{(n)} + H^{(1)} \Phi^{(n-1)} = \sum_{m=0}^n \Phi^{(n-m)} \mathcal{E}^{(m)}, \quad n \geq 1. \quad (2.22)$$

It is convenient to define the sequence of partial sums,

$$\begin{aligned} \Phi(N) &= \sum_{n=0}^N \lambda^n \Phi^{(n)}, \\ \mathcal{E}(N) &= \sum_{n=0}^N \lambda^n \mathcal{E}^{(n)}, \end{aligned} \quad (2.23)$$

and the sequence of secular equations

$$|\langle \Phi(N) | H - E | \Phi(N) \rangle| = 0. \quad (2.24)$$

The perturbation equations allow Eq. (2.24) to be written

$$0 = |\langle \Phi(N) | H - E | \Phi(N) \rangle| =$$

$$\left\{ \begin{aligned} & \langle \Phi(N) | \Phi(N) \rangle (E(N) - E) \\ & + \lambda^{N+1} \sum_{n=0}^{N-1} \lambda^n \left\{ \langle \Phi^{(n)} | H^{(1)} | \Phi^{(N)} \rangle \right. \\ & \quad \left. - \sum_{p=0}^n \sum_{q=0}^{N+p-n-1} \langle \Phi^{(p)} | \Phi^{(n+1-p+q)} \rangle E^{(N-p)} \right\} \\ & + \lambda^{2N+1} \sum_{n=0}^{N-1} \lambda^n \left\{ \langle \Phi^{(N)} | H^{(1)} | \Phi^{(N)} \rangle \delta_{n0} \right. \\ & \quad \left. - \sum_{p=0}^{N-n-1} \sum_{q=0}^p \langle \Phi^{(n+p+1)} | \Phi^{(N-p+q)} \rangle E^{(N-p)} \right\} \end{aligned} \right\} \quad (2.25)$$

This formula is derived in Appendix B.

Thus, the total Eqs. (2.13) and (2.15) are replaced by the perturbation equations (2.22) and the secular equations (2.24). The eigenvalues and eigenvectors of Eq. (2.24) for successively greater values of N provide a sequence of eigensolutions which, assuming convergence, approaches the exact solutions (E_k, Ψ_k) .

Normalization conditions and the choice of the transformation \mathbb{C} must be given to fully specify $\Phi^{(n)}$ and $E^{(n)}$. The normalization of Φ_k is completely determined by \mathbb{C} and Eq. (2.12), assuming that

the original functions Ψ_k are normalized. According to Eq. (2.14) the rows of \mathbb{C} are eigenvectors of \mathbb{E} corresponding to the eigenvalues E_k . Thus, if none of the energies E_k is degenerate, the specification of \mathbb{E} uniquely fixes \mathbb{C} and, hence, the normalization of Φ .

Relations to fix \mathbb{E} are given separately for degenerate and almost degenerate problems in the next two Sections. It can be anticipated that \mathbb{C} cannot be chosen in a non-arbitrary manner, since any set of S functions which satisfies Eq. (2.13) and (2.21) is sufficient to determine the solutions (E_k, Ψ_k) . This is not to say that the choice of \mathbb{C} does not have important consequences. A particular choice is $\mathbb{C} = 1$, in which case the formalism reduces to a Rayleigh-Schrödinger development for each state (E_k, Ψ_k) separately. As the previous discussion has suggested, and as later discussions will make explicit, other choices of \mathbb{C} are advantageous in treating degenerate and almost degenerate problems.

Nevertheless, in case that the Rayleigh-Schrödinger expansion of (E_k, Ψ_k) is possible, the present formalism, based on Eq. (2.13), (2.15), and any non-singular \mathbb{C} , is equivalent. More precisely, it can be shown that the roots of the secular equation (2.24) are the exact energies E_k , plus terms $O(\lambda^{2N+2})$, regardless of the choice of \mathbb{C} . Thus, if the eigenvalues and vectors of Eq. (2.24) are expanded in powers of λ for successive values of N , the unique asymptotic expansion of (E_k, Ψ_k) is obtained.

The proof of the underlined statement is contained in the derivation which led to Eq. (2.17). If $H\Phi(N) = \Phi(N)E(N) + O(\lambda^{N+1})$

and $\chi(N)$ is any basis for the space orthogonal to $\Phi(N)$, then the interaction elements $\langle \Phi(N) | H | \chi(N) \rangle$ are $O(\lambda^{N+1})$, irrespective of the values of $\mathcal{E}(N)$. Hence if the dimension of the secular equation (2.24) is increased to include $\chi(N)$, the original eigenvalues are affected by $O(\lambda^{2N+2})$. Since the inclusion of $\chi(N)$ leads to exact energies of H , it follows that the roots of Eq. (2.24) are accurate through $O(\lambda^{2N+1})$.

Eq. (2.24) can also be thought of as arising from the use of the variational method with the linear variational function

$$\tilde{\Psi} = \sum_{k=1}^S \Phi_k(N) \tilde{a}_k,$$

where the \tilde{a}_k are variational parameters. In this connection, the Hylleraas-Undheim theorem⁵¹ is relevant: if the roots of Eq. (2.24) are arranged in ascending order, they provide successive upper bounds to the corresponding exact energy eigenvalues of H of the same symmetry. Thus, in case that the states in \mathcal{S} are the lowest states of H corresponding to particular symmetries, the roots of Eq. (2.24) are upper bounds to the energies which they approximate.

An alternative way to obtain energies which are accurate through $O(\lambda^{2N+1})$, but which are not necessarily upper bounds to exact eigenvalues, is to solve the secular equation

$$|\mathcal{E}(2N+1) - E| = 0, \quad (2.26)$$

where $\mathcal{E}(2N+1)$ is defined by Eq. (2.23). The roots of Eq. (2.26) are the exact energies E_k , $1 \leq k \leq S$, accurate through $O(\lambda^{2N+1})$ regardless of the choice of \mathcal{C} . This follows from Eq. (2.25) with

N replaced by $2N+1$. Then the sums in Eq. (2.25) are $O(\lambda^{2N+2})$ and hence may be neglected without affecting the roots except in $O(\lambda^{2N+2})$. Factoring $\langle \Phi(2N+1) | \tilde{\Phi}(2N+1) \rangle$ from Eq. (2.25) yields Eq. (2.26).

The analog of the secular equation (2.26) in the usual Rayleigh-Schrödinger theory is the partial sum of the perturbation energies, as defined by Eq. (2.9). The secular equation (2.24) corresponds to the expectation value of H with the wavefunction accurate through $O(\lambda^N)$. Even in the Rayleigh-Schrödinger theory, it is difficult to say which way of computing the energy is more accurate.⁶⁹ In any case, the roots of Eq. (2.24) differ from those of Eq. (2.26) by $O(\lambda^{2N+2})$.

With these general results established, it is convenient to consider separately the degenerate and almost degenerate cases in order to derive relations to fix the elements of \mathcal{C} .

2.3 Degenerate Perturbation Theory.

For a degenerate perturbation problem, the special set of states $\Phi^{(0)}$ is defined to be any linearly independent set which spans precisely the same space as the S' eigenfunctions of the S -fold degenerate level of the unperturbed hamiltonian

$$(H^{(0)} - \epsilon^{(0)}) \phi_k^{(0)} = 0, \quad 1 \leq k \leq S'. \quad (2.27)$$

It is convenient to choose the $\Phi^{(0)}$ to be orthonormal

$$\langle \Phi^{(0)} | \Phi^{(0)} \rangle = 1, \quad (2.28)$$

but it is not necessary to assume any other special properties.

Eq. (2.27) implies that in Eq. (2.22) $\mathcal{E}^{(0)} = \epsilon^{(0)} \mathbf{1}$. The knowledge of $\mathcal{E}^{(0)}, \phi^{(0)}$ allows each term $\mathcal{E}^{(n)}, \phi^{(n)}$ to be determined successively. The energies $\mathcal{E}^{(n)}$ are fixed by requiring each perturbation equation (2.22) to be mathematically consistent: for a general inhomogeneous partial differential equation to possess a solution, the inhomogeneity must be orthogonal to all solutions of the homogeneous equation. In the present example, the homogeneous equation is (2.27), so that the consistency condition is

$$\langle \phi^{(0)} | H^{(1)} | \phi^{(n-1)} \rangle = \sum_{k=1}^n \langle \phi^{(0)} | \phi^{(n-k)} \rangle \mathcal{E}^{(k)},$$

or

$$\mathcal{E}^{(n)} = \langle \phi^{(0)} | H^{(1)} | \phi^{(n-1)} \rangle - \sum_{k=1}^{n-1} \langle \phi^{(0)} | \phi^{(n-k)} \rangle \mathcal{E}^{(k)} \quad (2.29)$$

With the $\mathcal{E}^{(n)}$ thus defined, the functions $\phi^{(n)}$ are obtained by solving the Eqs. (2.22). It should be noted, however, that the components $\langle \phi^{(0)} | \phi^{(n)} \rangle$ are not fixed by any of these equations. This is analogous to the non-degenerate case where the indeterminacy is due to the arbitrariness of the normalization and phase of the total wavefunction.⁵² The underlined theorem on page 24, that the roots of Eq. (2.24) are invariant to \mathcal{C} through $O(\lambda^{2N+1})$, implies that $\langle \phi^{(0)} | \phi^{(n)} \rangle$ may be fixed in any consistent manner. A general approach is to leave the integrals $\langle \phi_R^{(0)} | \phi_L^{(n)} \rangle$ as undetermined parameters in $\Phi^{(n)}$ to be fixed by minimizing the roots of the secular equation (2.24). This procedure is developed in more detail in Section 2.4 in connection with the almost degenerate case.

In the present Section it is convenient to fix $\langle \phi^{(\omega)} | \phi^{(n)} \rangle$ by the full normalization condition (cf. Eq. (2.8)),

$$\left. \begin{aligned} \sum_{k=0}^n \langle \phi^{(k)} | \phi^{(2n+1-k)} \rangle &= 0 \\ \sum_{k=0}^{n-1} \langle \phi^{(k)} | \phi^{(2n-k)} \rangle &= -\frac{1}{2} \langle \phi^{(n)} | \phi^{(n)} \rangle \end{aligned} \right\} n > 0. \quad (2.30)$$

This choice of normalization has the properties that

- i) $\langle \Phi | \Phi \rangle = 1$; this follows simply by expanding $\langle \Phi | \Phi \rangle$ in powers of λ and using Eq. (2.28) and (2.30);
- ii) \mathbb{E} is a hermitean matrix; this follows from i and Eq. (2.13), i.e.,

$$\langle \Phi | H | \Phi \rangle = \langle \Phi | \Phi \rangle \mathbb{E} = \mathbb{E}. \quad (2.31)$$

The first member of Eq. (2.31) is hermitean; hence the last is also.

In Appendix B, it is shown that the perturbation terms $\mathbb{E}^{(n)}$ are also hermitean. Intermediate normalization, $\langle \phi^{(\omega)} | \Phi \rangle = 1$, leads to a nonhermitean \mathbb{E} ;

- iii) the knowledge of Φ accurate through $O(\lambda^n)$ is sufficient to compute \mathbb{E} accurate through $O(\lambda^{2n+2})$. This is the analog of the Wigner theorem and follows from the formulas

$$\begin{aligned}
\mathbb{E}^{(2n+1)} &= \langle \phi^{(n)} | H^{(1)} | \phi^{(n)} \rangle \\
&- \frac{1}{2} \sum_{k=1}^n \sum_{\ell=0}^{k-1} \left\{ \mathbb{E}^{(k)} \langle \phi^{(n+\ell+1-k)} | \phi^{(n-\ell)} \rangle + \langle \phi^{(n-\ell)} | \phi^{(n+\ell+1-k)} \rangle \mathbb{E}^{(k)} \right\} \\
&- \frac{1}{2} \sum_{k=2}^n \sum_{\ell=0}^{\left\{ \frac{k}{2} \right\}} \mathbb{E}^{(k)} \left\{ \langle \phi^{(n+\ell+1-k)} | \phi^{(n-\ell)} \rangle - \langle \phi^{(n-\ell)} | \phi^{(n+\ell+1-k)} \rangle \right\} \\
&+ \frac{1}{2} \sum_{k=2}^n \sum_{\ell=0}^{\left\{ \frac{k}{2} \right\}} \left\{ \langle \phi^{(n+\ell+1-k)} | \phi^{(n-\ell)} \rangle - \langle \phi^{(n-\ell)} | \phi^{(n+\ell+1-k)} \rangle \right\} \mathbb{E}^{(k)},
\end{aligned}
\tag{2.32}$$

where $\left\{ \frac{k}{2} \right\} = \begin{cases} \frac{k-2}{2}, & k \text{ even} \\ \frac{k-3}{2}, & k \text{ odd}; \end{cases}$

$$\begin{aligned}
\mathbb{E}^{(2n)} &= \frac{1}{2} \left\{ \langle \phi^{(n-1)} | H^{(1)} | \phi^{(n)} \rangle + \langle \phi^{(n)} | H^{(1)} | \phi^{(n-1)} \rangle \right\} \\
&- \frac{1}{2} \sum_{k=1}^n \sum_{\ell=0}^{k-1} \left\{ \mathbb{E}^{(k)} \langle \phi^{(n-\ell)} | \phi^{(n-k+\ell)} \rangle + \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle \mathbb{E}^{(k)} \right\} \\
&- \frac{1}{2} \sum_{k=1}^{n-1} \sum_{\ell=0}^{\left[\frac{k}{2} \right]} \mathbb{E}^{(k)} \left\{ \langle \phi^{(n-\ell)} | \phi^{(n-k+\ell)} \rangle - \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle \right\} \\
&+ \frac{1}{2} \sum_{k=1}^{n-1} \sum_{\ell=0}^{\left[\frac{k}{2} \right]} \left\{ \langle \phi^{(n-\ell)} | \phi^{(n-k+\ell)} \rangle - \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle \right\} \mathbb{E}^{(k)},
\end{aligned}
\tag{2.33}$$

where $\left[\frac{k}{2} \right] = \begin{cases} \frac{k-2}{2}, & k \text{ even} \\ \frac{k-1}{2}, & k \text{ odd.} \end{cases}$

For $n = 0, 1$, recall the convention stated following Eq. (2.5).

These formulas are derived in Appendix B by algebraic manipulations of Eqs. (2.22), (2.29), and (2.30) in a manner completely analogous to nondegenerate theory.⁵²

It is at first sight surprising that Eq. (2.32) and (2.33) depend on a particular choice of normalization, in view of the proof on page 24 that $\Phi(N)$ is sufficient to compute the energies E_k , accurate through $O(\lambda^{2N+1})$, regardless of the normalization. There is no conflict in the two results, however, since, for example, the off-diagonal elements of $\mathbb{C}^{(2N+1)}$ do not contribute to the roots of Eq. (2.24) through $O(\lambda^{2N+1})$.

Solution of the Perturbation Equations. The n-th order perturbation equation (2.22) may be solved exactly in terms of the eigenfunctions of the unperturbed hamiltonian $H^{(0)}$. This is facilitated by the introduction of the reduced resolvent,

$$R^{(0)} = \sum_k' \frac{|\phi_k^{(0)}\rangle \langle \phi_k^{(0)}|}{\epsilon^{(0)} - \epsilon_k^{(0)}}$$

where the prime on the summation means that all the members in $\phi^{(0)}$ are to be excluded from the sum. Otherwise, the sum is over a complete set of eigenstates of $H^{(0)}$. It may be readily shown that

$$R^{(0)} \phi^{(0)} = 0,$$

$$(H^{(0)} - \epsilon^{(0)}) R^{(0)} = |\phi^{(0)}\rangle \langle \phi^{(0)}| - I$$

In terms of $R^{(0)}$ the solutions of the perturbation equations which satisfy the normalization conditions (2.30) may be written

$$\phi^{(n)} = R^{(0)} \{ H^{(1)} \phi^{(n-1)} - \sum_{k=1}^{n-1} \phi^{(n-k)} \epsilon^{(k)} \} + \phi^{(0)} N^{(n)}, \quad (2.34)$$

where the matrix $N^{(n)}$ is determined by requiring that $\phi^{(n)}$ satisfy the normalization conditions Eq. (2.30). The explicit formula for $N^{(n)}$ is, in terms of lower order functions,

$$N^{(2n+1)} = - \sum_{k=1}^n \langle \phi^{(k)} | \phi^{(2n+1-k)} \rangle, \quad (2.35)$$

and

$$N^{(2n)} = -\frac{1}{2} \langle \phi^{(n)} | \phi^{(n)} \rangle - \sum_{k=1}^{n-1} \langle \phi^{(k)} | \phi^{(2n-k)} \rangle.$$

That $\phi^{(n)}$ defined by Eq. (2.34) actually solves the perturbation equation (2.22) and the normalization condition (2.30) is easily verified by substitution.

Except for simple examples, the expressions given above are of formal interest only, since the summations over excited states cannot be evaluated. In general, however, it is possible to obtain variational approximations to $\phi^{(n)}$. For example, the first-order functions may be determined by finding the stationary points of the functionals

$$\begin{aligned} J_k[\tilde{\phi}_k^{(1)}] &= \langle \tilde{\phi}_k^{(1)} | H^{(0)} - \epsilon^{(0)} | \tilde{\phi}_k^{(1)} \rangle + \langle \tilde{\phi}_k^{(1)} | H^{(1)} | \phi_k^{(0)} \rangle \\ &+ \langle \phi_k^{(0)} | H^{(1)} | \tilde{\phi}_k^{(1)} \rangle - \sum_{\ell=1}^S \left\{ \langle \tilde{\phi}_k^{(1)} | \phi_\ell^{(0)} \rangle + \langle \phi_\ell^{(0)} | \tilde{\phi}_k^{(1)} \rangle \right\} \epsilon_{k\ell}^{(1)}, \end{aligned}$$

where $\tilde{\phi}_k^{(1)}$ is a trial function corresponding to the exact function $\phi_k^{(1)}$ which belongs to $\phi^{(1)}$. It is evident that if δJ_k vanishes for arbitrary variations $\delta \tilde{\phi}_k^{(1)}$ in $\tilde{\phi}_k^{(1)}$, then $\tilde{\phi}_k^{(1)}$ satisfies Eq. (2.22) for $n=1$. This is analogous to the Hylleraas

variational method in non-degenerate Rayleigh-Schrödinger perturbation theory.^{58,52}

Calculation of the Energy. Given the solutions of the first N perturbation equations (2.22), energies accurate through $O(\lambda^{2N+1})$ are obtained by solving either the secular equation (2.24) or the secular equation (2.26).

As discussed previously, in case that the states in \mathcal{H} are the lowest energy states of H , the best approximations to the exact energies E_R obtainable from Eq. (2.24) result from minimizing the roots with respect to the integrals $\langle \phi^{(0)} | \phi^{(n)} \rangle$. It was also shown, however, that these roots differ by $O(\lambda^{2N+2})$ from the roots obtained using the full normalization condition Eq. (2.30). Then in particular cases, Eq. (2.25) simplifies considerably. For $N=1$ and full normalization, the secular equation (2.24) becomes

$$0 = |\langle \Phi^{(1)} | H - E | \Phi^{(1)} \rangle| =$$

$$\left| \begin{aligned} & (1 + \lambda^2 \langle \phi^{(1)} | \phi^{(1)} \rangle) (\epsilon^{(0)} + \lambda \epsilon^{(1)} - E) \\ & + \lambda^2 \epsilon^{(2)} + \lambda^3 \epsilon^{(3)} \\ & + \frac{1}{2} \lambda^3 [\epsilon^{(1)}, \langle \phi^{(1)} | \phi^{(1)} \rangle] \end{aligned} \right| \quad (2.36)$$

The roots of Eq. (2.36) are accurate through $O(\lambda^3)$.

Alternatively, the energy may be obtained as a root of Eq. (2.26), which is easier to apply than Eq. (2.24) because the matrix elements are simpler and E appears only on the diagonal. The matrix $G(2N+1)$ may be diagonalized by a unitary transformation $U(N)$ to give S

eigenvalues E_R , accurate through $O(\lambda^{2N+1})$, and corresponding eigenfunctions $\Psi(N) = \Phi(N) C(N)^\dagger$, accurate through $O(\lambda^N)$.

For $N=1$, it may be verified explicitly that the roots of Eq. (2.24) differ by $O(\lambda^{2N+2})$ from the roots of Eq. (2.26). Factoring $(1 + \lambda^2 \langle \Phi^{(1)} | \Phi^{(1)} \rangle)$ from Eq. (2.36) yields

$$0 = | \langle \Phi^{(1)} | H - E | \Phi^{(1)} \rangle | =$$

$$| 1 + \lambda^2 \langle \Phi^{(1)} | \Phi^{(1)} \rangle | \left| \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} + \lambda^2 \mathcal{E}^{(2)} + \lambda^3 \mathcal{E}^{(3)} - E \right.$$

$$\left. + \frac{1}{2} \lambda^3 [\mathcal{E}^{(1)}, \langle \Phi^{(1)} | \Phi^{(1)} \rangle] + O(\lambda^4) \right|$$

or

$$| \mathcal{E}^{(3)} - E + \frac{1}{2} \lambda^3 [\mathcal{E}^{(1)}, \langle \Phi^{(1)} | \Phi^{(1)} \rangle] + O(\lambda^4) | = 0.$$

When $\mathcal{E}^{(1)}$ is diagonal, the diagonal elements of the commutator vanish, so that the commutator does not contribute to the eigenvalues through $O(\lambda^3)$. Hence the roots of Eq. (2.36) agree with the eigenvalues of $\mathcal{E}^{(3)}$ through $O(\lambda^3)$.

Connections with other Degenerate Perturbation Formalisms. The first order perturbation equation (2.22) is equivalent to the first order equation of Van Vleck degenerate perturbation theory³⁶ and of the treatments of Kato³⁷ and Block.³⁸ For example, in Kato's method, one solves

$$| \langle \Phi^{(0)} | H_a - E K_a | \Phi^{(0)} \rangle | = 0,$$

where

$$H_a = E^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(1)} R^{(0)} H^{(1)} + \dots,$$

and

$$K_a = 1 - \lambda^2 H^{(1)} (R^{(0)})^2 H^{(1)} + \dots,$$

which is seen to be equivalent to Eq. (2.36) through $O(\lambda^2)$. Thus the present formalism represents an extension of these methods to arbitrary order.

If the secular equation (2.24) or (2.26) is solved by expansion in powers of λ , the usual Rayleigh-Schrödinger perturbation theory for the states in \mathcal{S} is obtained. One must then determine the correct zeroth order wavefunctions, which depend on the order in which the degeneracy is lifted. Hirschfelder⁴¹ has given a very thorough discussion of the complicated equations which result. The present formalism is much simpler because it does not contemplate the expansion of the secular equation, which may be solved by other procedures.⁶⁰

The connection of the present formalism with the partitioning technique for degenerate problems is considered in Appendix C. It is shown that the secular equation (2.26) results from a factorization of the corresponding partitioned secular equation which leaves the roots invariant through $O(\lambda^{2N+1})$. For $N > 1$, Eq. (2.26) is simpler to solve because the partitioned secular equation contains the energy E in a nonlinear fashion.

2.4 Almost-Degenerate Perturbation Theory.

For an almost-degenerate perturbation problem, the special set of states $\phi_k^{(0)}$ is defined to be S states $(\epsilon_k^{(0)}, \phi_k^{(0)})$ of the unperturbed hamiltonian,

$$(H^{(0)} - \epsilon_k^{(0)}) \phi_k^{(0)} = 0,$$

which are almost degenerate in the sense that the ratios (see Eq.(2.10))

$$\frac{\langle \phi_k^{(0)} | H^{(1)} | \phi_{k'}^{(0)} \rangle}{\epsilon_k^{(0)} - \epsilon_{k'}^{(0)}}, \quad 1 \leq k, k' \leq S,$$

are large. For simplicity, it is assumed that each of the levels $\epsilon_k^{(0)}$ is itself non-degenerate and that $\langle \phi_k^{(0)} | \phi_k^{(0)} \rangle = 1$.

Again the general equations to be solved are Eqs. (2.22) and (2.24) or (2.26). These equations are similar to the degenerate case, except that now $\mathcal{E}^{(0)}$ is diagonal but it is not a multiple of the unit matrix. Furthermore, the perturbation energies are not fixed by requirements of mathematical consistency. To see this, consider the first order equation (2.22) for the component $\phi_k^{(1)}$:

$$(H^{(0)} - \epsilon_k^{(0)}) \phi_k^{(1)} + H^{(1)} \phi_k^{(0)} = \sum_{j=1}^S \phi_j^{(0)} \epsilon_{jk}^{(1)}. \quad (2.37)$$

The only general condition to fix the $\epsilon_{jk}^{(1)}$ is that the inhomogeneity must be orthogonal to the eigenfunctions of $H^{(0)}$ with energy $\epsilon_k^{(0)}$. By assumption, this consists of the single function $\phi_k^{(0)}$; hence, multiplying Eq. (2.37) by $\phi_k^{(0)*}$ and integrating yields

$$\epsilon_{kk}^{(1)} = \langle \phi_k^{(0)} | H^{(1)} | \phi_k^{(0)} \rangle.$$

That is, only the diagonal elements of $\mathcal{E}^{(1)}$ (and, in general, \mathcal{E}) are determined.

Thus the off-diagonal elements of \mathcal{E} are not fixed by the formalism. Each choice of these numbers results in a different expansion of Φ and \mathcal{E} . Although the roots of the secular equation (2.21) obtained by different choices differ only by "higher-order terms", it is of interest to examine various ways of fixing the off-diagonal elements of \mathcal{E} .

The DE-FOP-VIM Formalism.³⁹ A general method of handling the indeterminacy in \mathcal{E} is to solve for each $\phi^{(n)}$ as an implicit function of the off-diagonal elements $\epsilon_{jk}^{(n)}$. Then these quantities can be determined by minimizing the roots of the secular equation (2.24) with respect to variations in the $\epsilon_{jk}^{(n)}$.

To gain insight into this procedure, consider the solution of Eq. (2.37) with $\epsilon_{jk}^{(1)}$, $j \neq k$, arbitrary. The general solution may be written

$$\hat{\phi}_k^{(1)} = \phi_k^{(1)} + \sum_{j \neq k}^S \phi_j^{(0)} \left[\frac{\langle \phi_j^{(0)} | H^{(1)} | \phi_k^{(0)} \rangle - \epsilon_{jk}^{(1)}}{\epsilon_k^{(0)} - \epsilon_j^{(0)}} \right] + a_k^{(1)} \phi_k^{(0)},$$

where $\phi_k^{(1)}$ satisfies

$$(H^{(0)} - \epsilon_k^{(0)})\phi_k^{(1)} + H^{(1)}\phi_k^{(0)} = \sum_{j=1}^S \phi_j^{(0)} \langle \phi_j^{(0)} | H^{(1)} | \phi_k^{(0)} \rangle,$$

$$\langle \phi_k^{(1)} | \phi_j^{(0)} \rangle = 0, \quad 1 \leq j \leq S,$$

and $a_k^{(1)}$ is an arbitrary normalization constant. Then the S -dimensional variational basis set

$$\Phi_k^{(1)} = \phi_k^{(0)} + \lambda \hat{\phi}_k^{(1)}, \quad 1 \leq k \leq S,$$

which leads to the $S \times S$ secular equation (2.36) with $\phi^{(1)}$ replaced by $\hat{\phi}^{(1)}$, is clearly equivalent to the $2S$ -dimensional basis

$$\left. \begin{array}{c} \phi_k^{(0)} \\ \phi_k^{(1)} \end{array} \right\}, \quad 1 \leq k \leq S.$$

This leads to the $2S \times 2S$ secular equation

$$0 = \begin{vmatrix} \langle \phi^{(0)} | H - E | \phi^{(0)} \rangle & \langle \phi^{(0)} | H - E | \phi^{(1)} \rangle \\ \langle \phi^{(1)} | H - E | \phi^{(0)} \rangle & \langle \phi^{(1)} | H - E | \phi^{(1)} \rangle \end{vmatrix}. \quad (2.39)$$

S roots of Eq. (2.39) are identical to the roots of Eq. (2.36) if in the latter equation the $\epsilon_{jk}^{(1)}$ and $a_k^{(1)}$ are varied freely and independently to a stationary point.

The Eq. (2.39) appears also in Hirschfelder's DE-VOP-VIM formalism³⁹ for degenerate and almost-degenerate perturbation problems. It is easily seen that the extension to N -th order of this method of choosing \mathcal{E} leads to an $(N+1)S \times (N+1)S$ secular equation, S roots of which give the desired energies accurate through $O(\lambda^{2N+1})$.

The DE-FOP-VIM method is simplest to apply in case that the states k in \mathcal{S} are the lowest energy states of H corresponding to particular symmetries. Then, by Hylleraas-Undheim theorem, the S smallest roots of the DE-FOP-VIM secular equation can be identified as the approximations to the corresponding exact energies. In case that there are lower energy states of H than the states in \mathcal{S} , the interpretation of the roots of the DE-FOP-VIM secular equation can become ambiguous. Clearly, the DE-FOP-VIM procedure cannot be applied to the secular equation (2.26) since this equation cannot be derived from the variational method.

The Kirtman Formalism.⁴⁰ Another method of choosing the off-diagonal elements of \mathcal{E} is by analogy with the degenerate case. The full normalization conditions (2.30) uniquely fix all elements of \mathcal{E} , just as in the degenerate case. Furthermore, in the present case \mathcal{E} is hermitean and the formulas (2.32) and (2.33) for $\mathcal{E}^{(n)}$ continue to hold if the wavefunction is required to satisfy Eq. (2.30).

This method of fixing \mathcal{E} was first discussed by Kirtman⁴⁰ in his extension of Van Vleck degenerate perturbation theory to the almost degenerate case. Kirtman considered in detail the calculation of the energy through third order, which in his formalism is given as a root of the secular equation

$$\begin{aligned}
 & \left. \begin{aligned}
 & \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} - E \\
 & + \lambda^2 \left\{ \langle \phi^{(0)} | H^{(0)} | \phi^{(0)} \rangle - \frac{1}{2} \mathcal{E}^{(0)} \langle \phi^{(1)} | \phi^{(1)} \rangle - \frac{1}{2} \langle \phi^{(0)} | \phi^{(1)} \rangle \mathcal{E}^{(0)} \right. \\
 & \quad \left. + \langle \phi^{(0)} | H^{(0)} | \phi^{(1)} \rangle + \langle \phi^{(0)} | H^{(1)} | \phi^{(0)} \rangle \right\} \\
 & + \lambda^3 \left\{ \langle \phi^{(0)} | H^{(1)} | \phi^{(1)} \rangle - \frac{1}{2} \mathcal{E}^{(0)} \langle \phi^{(1)} | \phi^{(1)} \rangle - \frac{1}{2} \langle \phi^{(0)} | \phi^{(1)} \rangle \mathcal{E}^{(0)} \right\}
 \end{aligned} \right\} \quad (2.40)
 \end{aligned}$$

The first order equation (2.22) and Eqs. (2.32) and (2.33) can be used to simplify Eq. (2.40) to

$$\left| \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} + \lambda^2 \mathcal{E}^{(2)} + \lambda^3 \mathcal{E}^{(3)} - E \right| = 0, \quad (2.41)$$

which is Eq. (2.26) for $N = 1$.

Hence the Kirtman formalism will denote the treatment of almost degenerate perturbation problems by the secular equation (2.26) with the full normalization conditions (2.30).

The modified Kirtman formalism will be used to label the treatment based on the secular equation (2.24) with the full normalization conditions (2.30).

The advantage of the Kirtman or modified Kirtman formalism is that the energy is obtained as a root of an $S \times S$ secular equation, rather than the $(N+1)S \times (N+1)S$ secular equation for the DE-FOP-VIM formalism. The roots of the DE-FOP-VIM secular equation are necessarily more accurate than the corresponding roots of the modified

Kirtman secular equation in case that the lowest energy states of H are being treated. In any case the corresponding roots of the three different equations differ by $O(\lambda^{2N+2})$. Thus, if the almost degenerate block of states is well separated from the remaining unperturbed states, the energies obtained by the three methods differ by terms which are, by hypothesis, negligible.

Transformation to an Exactly Degenerate Problem, The lack of uniqueness of the off-diagonal elements of \mathcal{E} can be avoided by defining a new split of H into an unperturbed hamiltonian and a perturbation, such that the unperturbed limit is exactly degenerate. In some cases there is a natural choice for the new unperturbed hamiltonian and eigenfunctions. In general it is possible to define

$$\bar{H}^{(0)} = H^{(0)} + |\phi^{(0)}\rangle [\bar{\mathcal{E}}^{(0)} - \mathcal{E}^{(0)}] \langle \phi^{(0)}|,$$

and

$$\bar{H}^{(1)} = \lambda H^{(1)} + |\phi^{(0)}\rangle [\mathcal{E}^{(0)} - \bar{\mathcal{E}}^{(0)}] \langle \phi^{(0)}|,$$

where

$$\bar{\mathcal{E}}^{(0)} = \bar{\mathcal{E}}^{(0)} 1,$$

and $\bar{\mathcal{E}}^{(0)}$ is an average unperturbed energy; e.g.,

$$\bar{\mathcal{E}}^{(0)} = S^{-1} \sum_{k=1}^S \mathcal{E}_k^{(0)}$$

Then all of the states $\Phi^{(0)}$ are exactly degenerate with respect to $\bar{H}^{(0)}$

$$(\bar{H}^{(0)} - \bar{E}^{(0)}) \Phi^{(0)} = 0, \quad (2.42)$$

so that the formalism of Section 2.3 can be applied. This method of handling almost-degeneracy is suggested in most textbooks.⁴⁸

Let a bar denote perturbation terms in the expansion of $\bar{\Phi}$ and \bar{E} based on Eq. (2.42);

$$\bar{\Phi} = \Phi^{(0)} + \bar{\Phi}^{(1)} + \dots,$$

and

$$\bar{E} = \bar{E}^{(0)} + \bar{E}^{(1)} + \bar{E}^{(2)} + \dots.$$

Through first order, $\bar{E}^{(0)}$ does not contribute to \bar{E} since, by Eq. (2.32),

$$\bar{E}^{(1)} = \langle \Phi^{(0)} | \bar{H}^{(1)} | \Phi^{(0)} \rangle = \lambda E^{(1)} + E^{(0)} - \bar{E}^{(0)}$$

so that

$$\bar{E}^{(0)} + \bar{E}^{(1)} = E^{(0)} + \lambda E^{(1)}.$$

With the normalization (2.30), $\langle \Phi^{(0)} | \bar{\Phi}^{(1)} \rangle = 0$, the first order equation (2.22) can be written

$$(H^{(0)} - \bar{E}^{(0)}) \bar{\Phi}^{(1)} + \lambda H^{(1)} \Phi^{(0)} = \lambda \Phi^{(0)} E^{(1)}.$$

Comparison with Eq. (2.37) reveals that $\bar{\epsilon}^{(0)}$ enters into $\bar{\Phi}^{(1)}$, and hence $\bar{\epsilon}^{(2)}$, in a non-trivial way, so that the latter quantities are not simply related to $\Phi^{(1)}$ and $\epsilon^{(2)}$. For this reason, development along these lines is not considered further here.

Solution of the Perturbation Equations. A formal solution to Eq. (2.22) may be given in terms of the resolvents

$$R_k^{(0)} = \sum_{\ell}' \frac{|\Phi_{\ell}^{(0)}\rangle \langle \Phi_{\ell}^{(0)}|}{\epsilon_k^{(0)} - \epsilon_{\ell}^{(0)}}, \quad 1 \leq k \leq S,$$

where again the prime means that no state belonging to $\Phi^{(0)}$ is included in the sum. This set of resolvents has the properties

$$R_k^{(0)} \Phi^{(0)} = 0,$$

$$(H^{(0)} - \epsilon_k^{(0)}) R_k^{(0)} = |\Phi^{(0)}\rangle \langle \Phi^{(0)}| - 1.$$

The solutions of the perturbation equations which satisfy the normalization conditions (2.30) may be written

$$\Phi_k^{(1)} = R_k^{(0)} H^{(1)} \Phi_k^{(0)},$$

$$\Phi_k^{(2)} = R_k^{(0)} \left\{ H^{(1)} \Phi_k^{(1)} - \sum_{\ell=1}^S \Phi_{\ell}^{(0)} \epsilon_{\ell k}^{(1)} \right\} - \frac{1}{2} \sum_{\ell=1}^S \Phi_{\ell}^{(0)} \langle \Phi_{\ell}^{(1)} | \Phi_k^{(1)} \rangle,$$

• • • ,

$$\Phi_k^{(n)} = R_k^{(0)} \left\{ H^{(1)} \Phi_k^{(n-1)} - \sum_{m=1}^{n-1} \sum_{\ell=1}^S \Phi_{\ell}^{(n-m)} \epsilon_{\ell k}^{(m)} \right\} - \sum_{\ell=1}^S \Phi_{\ell}^{(0)} N_{\ell k}^{(n)},$$

where $\Delta^{(n)}$ is given by Eq. (2.35). As in the degenerate case, variational principles may be given to allow the approximation of $\phi^{(n)}$ in practical calculations.⁴⁰

The relationship among the DE-FOP-VIM, Kirtman, and modified Kirtman formalisms is best understood by means of an example.

2.5 Example of Almost-degenerate Perturbation Theory.

The system⁶¹ of two coupled simple harmonic oscillators described by the hamiltonian

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} (1+\Delta)^2 x^2 + \frac{1}{2} (1-\Delta)^2 y^2 + \lambda xy$$

provides a nice illustration of the formalism developed in the preceding sections. The Schrödinger equation for this case is exactly solvable, and the eigenenergies are

$$\begin{aligned} E_{nm} &= (n + \frac{1}{2}) \omega_+ + (m + \frac{1}{2}) \omega_- \\ &= \frac{1}{2} (n + m + 1) (\omega_+ + \omega_-) + \frac{1}{2} (n - m) (\omega_+ - \omega_-) \end{aligned} \quad (2.43)$$

where $n, m = 0, 1, 2, \dots$ and

$$\omega_{\pm} = \sqrt{1 + \Delta^2 \pm \sqrt{4\Delta^2 + \lambda^2}}$$

The theory will be applied to the almost degenerate $n=1, m=0$ and $n=0, m=1$ states. By squaring the sum and difference of ω_+ and ω_- , and then taking the square root of the result, one can derive

$$\omega_+ \pm \omega_- = \sqrt{2(1+\Delta^2) \pm 2\sqrt{(1-\Delta^2)^2 - \lambda^2}} \quad (2.44)$$

Perturbation theory corresponds to expanding the radicals in Eq. (2.44). Assuming that $\lambda \ll (1-\Delta^2)$ allows the inner radical to be expanded in powers of λ . For the upper sign, this assumption also permits the expansion of the outer radical. To expand the outer radical for the lower sign, however, requires a knowledge of the relative magnitude of λ , the perturbation, and Δ , the splitting between the frequencies. This is the characteristic feature of almost degenerate perturbation problems. At this point, the most general expansions possible are

$$E_{10} = 2 - \frac{\lambda^2}{4(1-\Delta^2)} + O(\lambda^4) \\ \pm \sqrt{\Delta^2 + \frac{\lambda^2}{4(1-\Delta^2)} + \frac{\lambda^4}{16(1-\Delta^2)^3} + O(\lambda^6)},$$

where the upper sign corresponds to 10; the lower, to 01.

The Rayleigh-Schrödinger treatment of this problem corresponds to expanding $\omega_+ - \omega_-$ in powers of λ , which clearly converges only for $\lambda < \Delta$. Nevertheless, through order λ^3 , the energies are given by

$$E_{10}^{(RS)} = 2 - \frac{\lambda^2}{4(1-\Delta^2)} \pm \Delta \pm \frac{\lambda^2}{8\Delta(1-\Delta^2)} \quad (2.45)$$

For the application of the formalism developed in the last section, the unperturbed hamiltonian is taken to be

$$H^{(0)} = -\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} (1+\Delta)^2 x^2 + \frac{1}{2} (1-\Delta)^2 y^2,$$

and the perturbation

$$H^{(1)} = xy.$$

The eigensolutions of the unperturbed problem are

$$E_{nm}^{(0)} = (n + \frac{1}{2})(1+\Delta) + (m + \frac{1}{2})(1-\Delta),$$

and

$$\phi_{nm}^{(0)} = u_n(x) u_m(y),$$

where u_n is a simple harmonic oscillator eigenfunction.

The theory will be applied to the states $n=1$, $m=0$ and

$n=0$, $m=1$ Hence,

$$E^{(0)} = \begin{pmatrix} 2+\Delta & 0 \\ 0 & 2-\Delta \end{pmatrix}$$

and

$$\phi^{(0)} = (\phi_{10}^{(0)}, \phi_{01}^{(0)})$$

The choice of the normalization condition Eq. (2.30) implies

$$\langle \phi^{(0)} | \phi^{(1)} \rangle = 0,$$

and the solution of the first order equation (2.22) yields

$$\phi^{(1)} = -[2\sqrt{2(1-\Delta^2)}]^{-1} (\phi_{21}^{(0)}, \phi_{12}^{(0)}),$$

$$\epsilon^{(1)} = \begin{pmatrix} 0 & \frac{1}{2\sqrt{1-\Delta^2}} \\ \frac{1}{2\sqrt{1-\Delta^2}} & 0 \end{pmatrix},$$

$$\epsilon^{(2)} = \begin{pmatrix} -\frac{1}{4(1-\Delta^2)} & 0 \\ 0 & -\frac{1}{4(1-\Delta^2)} \end{pmatrix},$$

$$\epsilon^{(3)} = \begin{pmatrix} 0 & \frac{1}{16[1-\Delta^2]^{3/2}} \\ \frac{1}{16[1-\Delta^2]^{3/2}} & 0 \end{pmatrix}.$$

To this order, the energy of the Kirtman formalism is given by the roots of the secular equation (2.41) which yields

$$E_{01}(K) = 2 - \frac{\lambda^2}{4(1-\Delta^2)} \pm \sqrt{\Delta^2 + \left[\frac{\lambda}{2(1-\Delta^2)^{1/2}} + \frac{\lambda^3}{16(1-\Delta^2)^{3/2}} \right]^2}. \quad (2.46)$$

Alternatively, the modified Kirtman secular equation (2.36) reduces for this case to

$$|(1 + \lambda^2 \langle \phi^{(1)} | \phi^{(1)} \rangle)(\epsilon^{(0)} + \lambda \epsilon^{(1)} - E) + \lambda^2 \epsilon^{(2)} + \lambda^3 \epsilon^{(3)}| = 0,$$

which has the roots

$$E_{10}^{(0)}(M\lambda) = 2 - \frac{2\lambda^2}{8(1-\Delta^2) + \lambda^2} \quad (2.47)$$

$$\pm \sqrt{\Delta^2 + \left[\frac{\lambda}{2(1-\Delta^2)^{1/2}} + \frac{\lambda^3}{2(1-\Delta^2)^{1/2} [8(1-\Delta^2) + \lambda^2]} \right]^2}$$

Since the 10 and 01 states are the lowest energy states with their symmetry, the roots (2.47) are upper bounds to the exact energies. Clearly, the roots (2.47) differ from the roots (2.46) by terms of order λ^4 .

For the application of DE-FOP-VIM to this example, the secular equation to be solved is Eq. (2.39) which can be shown to be equivalent to

$$|H - E S| = 0,$$

where

$$H = \begin{pmatrix} \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} & \lambda^2 \mathcal{E}^{(2)} & \\ & \frac{1}{2} [\mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)}] \langle \phi^{(1)} | \phi^{(1)} \rangle & \\ \lambda^2 \mathcal{E}^{(2)} & + \frac{1}{2} \langle \phi^{(1)} | \phi^{(1)} \rangle [\mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)}] & \\ & - \lambda^2 \mathcal{E}^{(2)} + \lambda^3 \mathcal{E}^{(3)} & \end{pmatrix}$$

Substituting in the proper quantities and transforming to an orthonormal set of functions yields

$$0 = | \Phi^{-1/2} H \Phi^{-1/2} - E I | =$$

$$\begin{vmatrix} 2 + \Delta - E & \frac{\lambda}{2(1-\Delta^2)^{1/2}} & -\frac{\lambda}{\sqrt{2}(1-\Delta^2)^{1/2}} & 0 \\ \frac{\lambda}{2(1-\Delta^2)^{1/2}} & 2 - \Delta - E & 0 & -\frac{\lambda}{\sqrt{2}(1-\Delta^2)^{1/2}} \\ -\frac{\lambda}{\sqrt{2}(1-\Delta^2)^{1/2}} & 0 & 4 + \Delta - E & \frac{\lambda}{(1-\Delta^2)^{1/2}} \\ 0 & -\frac{\lambda}{2(1-\Delta^2)^{1/2}} & -\frac{\lambda}{(1-\Delta^2)^{1/2}} & 4 - \Delta - E \end{vmatrix} \quad (2.48)$$

If this secular equation is now solved by the matrix version of the same formalism that was used to obtain Eq. (2.46) and (2.47) it can be verified that the identical result is obtained, except for "higher-order terms". Thus if the perturbation expansions (2.20) are rapidly converging, the 4x4 secular equation (2.48) yields only a small improvement in the accuracy of the energy over the 2x2 secular equations.

The various perturbation treatments are compared numerically in Table 2.1 for the splitting of the unperturbed frequencies $\Delta = 0.1$. As expected, the Rayleigh-Schrödinger result, Eq. (2.45), is very inaccurate for $\lambda > \Delta$. Of the other methods, the Kirtman formalism provides the best approximation, although the roots are not necessarily upper bounds to the exact energies. The DE-FOP-VIM results

must be more accurate than the modified Kirtman results since the states under consideration are the lowest energy states of the same symmetry.

TABLE 2.1: Errors in Perturbation Energies of Coupled Harmonic Oscillators.

| λ | | E(exact) Eq. 2.43 | E(approximate) - E(exact) | | | |
|--------------------|---------|----------------------|--------------------------------------|---------------------|---------------------------------|------------------------|
| | | | Rayleigh- Schrödinger Eq. 2.45 | Kirtman Eq. 2.46 | Modified Kirtman Eq. 2.47 | DE-FOP-VIM Eq. 2.48 |
| $\lambda < \Delta$ | 0.00000 | 2.10000 1.90000 | 0 0 | 0 0 | 0 0 | 0 0 |
| | 0.03980 | 2.10158 1.89762 | 0.00002 -0.00002 | 0.00000 0.00000 | 0.00000 0.00000 | 0.00000 0.00000 |
| | 0.07960 | 2.10611 1.89068 | 0.00029 -0.00028 | 0.00000 0.00000 | 0.00000 0.00000 | 0.00000 0.00000 |
| $\lambda = \Delta$ | 0.10000 | 2.10941 1.88552 | 0.00069 -0.00067 | 0.00001 0.00001 | 0.00001 0.00001 | 0.00001 0.00001 |
| | 0.11940 | 2.11306 1.87971 | 0.00134 -0.00131 | 0.00002 0.00002 | 0.00002 0.00002 | 0.00002 0.00002 |
| $\lambda > \Delta$ | 0.15920 | 2.12177 1.86532 | 0.00383 -0.00372 | 0.00005 0.00006 | 0.00007 0.00008 | 0.00006 0.00007 |
| | 0.19900 | 2.13166 1.84809 | 0.00834 -0.00809 | 0.00012 0.00014 | 0.00017 0.00019 | 0.00014 0.00017 |
| | 0.23880 | 2.14222 1.82844 | 0.01538 -0.01484 | 0.00025 0.00029 | 0.00034 0.00040 | 0.00028 0.00036 |
| | 0.27860 | 2.15311 1.80668 | 0.02529 -0.02428 | 0.00045 0.00056 | 0.00063 0.00076 | 0.00052 0.00069 |
| | 0.31840 | 2.16405 1.78300 | 0.03835 -0.03660 | 0.00077 0.00098 | 0.00107 0.00132 | 0.00087 0.00120 |
| | 0.35820 | 2.17483 1.75753 | 0.05477 -0.05193 | 0.00124 0.00161 | 0.00171 0.00217 | 0.00139 0.00199 |

* $\Delta = 0.1$; For each λ , the upper entry gives results for $n=1, m=0$ state: the lower entry, for the $n=0, m=1$ state.

III. EXCHANGE PERTURBATION THEORIES

The mathematical difficulties associated with the development of exchange perturbation theory have been discussed in Chapter One. It was shown that the concept of order of perturbation terms is not rigorous and that many different expansions of the wavefunction are possible. In Chapter Two the perturbation formalism for degenerate and almost degenerate problems was developed with the intention of using it as a guide for exchange perturbation theory in the present Chapter. The essential idea is to construct, by perturbation methods, a finite basis set for the expansion of the wavefunction. The basis is defined to have small hamiltonian matrix elements coupling the basis with any function which is orthogonal to the basis. The energy and properly symmetrized wavefunction are obtained by diagonalizing the hamiltonian in the finite basis. The advantage of this procedure is that the basis functions are not required to have the symmetry of the total wavefunction, but simply form a basis for a reducible representation of the symmetry group of the hamiltonian. This approach to exchange perturbation theory leads to the Hirschfelder-Silbey formalism.

To avoid the added complications which arise when even the separated atom wavefunctions are unknown, the treatment developed in this Chapter is limited to the interaction of hydrogen atoms.

3.1 The Interaction of Ground State Hydrogen Atoms.

Consider the interaction of two ground state hydrogen atoms, a and b , separated by a distance R . There are two molecular states which arise from this separated-atom state: $(^1E, ^3\Psi)$, the $^1\Sigma_g^+$

ground state; and $(^uE, ^u\Psi)$, the $^3\Sigma_u^+$ repulsive excited state. The exact spatial wavefunctions for these states satisfy

$$(H - \epsilon) \psi = 0,$$

and

$$A_i \psi = \epsilon \psi, \quad \epsilon = g \text{ or } u.$$

The hamiltonian H is defined by

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R},$$

and A_i is a symmetry projector defined by

$$A_g = \left(\frac{1 \pm P_{12}}{2}\right) \left(\frac{1 \pm P_{ab}}{2}\right) \left(\frac{1 \pm \sigma}{2}\right) \mathcal{O}_\Sigma.$$

The upper sign is for g symmetry; the lower, for u . P_{12} permutes the electron labels, P_{ab} permutes the nuclei labels, σ reflects the electronic coordinates across any plane which includes the inter-nuclear axis, and \mathcal{O}_Σ is the projection operator for the $M=0$ eigenfunction of the total azimuthal orbital angular momentum \mathcal{L}_z

$$\mathcal{O}_\Sigma = \prod_{M>0}^{\infty} \frac{M - \mathcal{L}_z}{M}$$

A_i is seen to be a compound projector for the symmetry group of H . The first factor in A_i projects onto the space of either singlet (upper sign) or triplet (lower sign) functions; the second,

onto either gerade or ungerade functions; the third, onto + functions; and the last factor projects onto the space of Σ functions.

Zeroth Order Primitive Functions. When the atoms are infinitely separated ($R \rightarrow \infty$), an exact wavefunction for the system is

$$\phi_i^{(0)} = a_o(1) b_o(2),$$

where a_o is a 1s orbital centered about nucleus a, and b_o is a 1s orbital centered about nucleus b. The subscript "1" indicates the arbitrary assignment of electron 1 to atom a and electron 2 to atom b. Because of the physical indistinguishability of electrons, $\phi_i^{(0)}$ is degenerate with the configuration "2",

$$\phi_2^{(0)} = P_{12} \phi_1^{(0)} = b_o(1) a_o(2)$$

in the sense that

$$\langle \phi_1^{(0)} | H | \phi_1^{(0)} \rangle = \langle \phi_2^{(0)} | H | \phi_2^{(0)} \rangle.$$

This is a different type of degeneracy from that discussed in Chapter Two in that $\phi_1^{(0)}$, $\phi_2^{(0)}$ are not degenerate eigenfunctions of the same unperturbed hamiltonian. In particular,

$$(H_1^{(0)} - \epsilon^{(0)}) \phi_1^{(0)} = 0, \quad (3.1)$$

where

$$H_1^{(0)} = h_a(1) + h_b(2) \quad ; \quad \epsilon^{(0)} = 2e_o; \quad (3.2)$$

and

$$h_a = -\frac{1}{2} \nabla^2 - \frac{1}{r_a}, \quad (3.3)$$

and e_0 is the energy of a ground state hydrogen atom ($= -\frac{1}{2}$ Hartree), but

$$(H_2^{(0)} - E^{(0)}) \phi_2^{(0)} = 0,$$

where

$$H_2^{(0)} = P_{12} H_1^{(0)} P_{12} = h_b(1) + h_a(2). \quad (3.4)$$

Eq. (3.2) and (3.4) give $H_1^{(0)} - H_2^{(0)} = \left(\frac{1}{r_{b1}} + \frac{1}{r_{a2}} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} \right)$.

In group theoretic language, $\phi_1^{(0)}$ and $\phi_2^{(0)}$ are "primitive functions", i.e., they are a basis for reducible representation of the symmetry group of H . Since $\phi_1^{(0)}$ and $\phi_2^{(0)}$ do not have pure symmetry, there is no Rayleigh-Schrödinger expansion of ${}^g\Psi$, ${}^u\Psi$ which starts from $\phi_1^{(0)}$, $\phi_2^{(0)}$ as the unperturbed states and produces a wavefunction that has the symmetry of the exact functions, order by order.

Heitler-London Wavefunctions.⁴³ The projectors A_g, A_u allow the construction of zeroth order functions which do have the symmetry of the exact wavefunction. Putting

$${}^g\Psi^{(0)} = \frac{A_g \phi_1^{(0)}}{\langle A_g \phi_1^{(0)} | A_g \phi_1^{(0)} \rangle^{1/2}} = \frac{a_0(1)b_0(2) + b_0(1)a_0(2)}{\sqrt{2} \langle \phi_1^{(0)} | 1 + P_{12} | \phi_1^{(0)} \rangle^{1/2}},$$

and

(3.5)

$$u \Psi^{(0)} = \frac{A_u \phi_1^{(0)}}{\langle A_u \phi_1^{(0)} | A_u \phi_1^{(0)} \rangle^{1/2}} = \frac{a_0(1) b_0(2) - b_0(1) a_0(2)}{\sqrt{2} \langle \phi_1^{(0)} | 1 - P_{12} | \phi_1^{(0)} \rangle^{1/2}},$$

yields the Heitler-London approximation to the wavefunctions. In perturbation theory, the energy through first order is simply the expectation value of H computed with the zeroth order wavefunction. Thus

$$^i E^{(0)} + ^i E^{(1)} = \langle ^i \Psi^{(0)} | H | ^i \Psi^{(0)} \rangle.$$

Eq. (3.1), (3.3), and (3.5) yield

$$^g E^{(0)} = ^u E^{(0)} = \epsilon^{(0)},$$

and

$$^g E^{(1)} = \frac{\langle \phi_1^{(0)} | (H - H_1^{(0)}) (1 \pm P_{12}) | \phi_1^{(0)} \rangle}{\langle \phi_1^{(0)} | 1 \pm P_{12} | \phi_1^{(0)} \rangle}$$

(3.6)

$$= \frac{V_{oo} \pm V'_{oo}}{1 \pm S_{oo}^2}$$

where

$$V_{oo} = \iint [a_o(1) b_o(2)]^2 \left[\frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{R} \right] d\tau_1 d\tau_2,$$

$$V'_{oo} = \iint a_o(1) b_o(1) a_o(2) b_o(2) \left[\frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{R} \right] d\tau_1 d\tau_2,$$

$$S_{oo} = \int a_o(1) b_o(1) d\tau_1. \quad (3.7)$$

The integrals in Eq. (3.7) are all well known.^{43,53}

It is not possible to proceed in a straightforward manner to higher order, however, since ${}^g\Psi^{(0)}$, ${}^u\Psi^{(0)}$ are not eigenfunctions of $H_1^{(0)}$ or $H_2^{(0)}$.

Exact Primitive Functions. On the other hand, given the exact spatial wavefunctions ${}^g\Psi$ and ${}^u\Psi$, it is possible to construct two exact primitive functions Φ_1 and Φ_2 which have precisely the same transformation properties as $\phi_1^{(0)}$ and $\phi_2^{(0)}$. That is,

$$\Phi_2 = P_{12} \Phi_1, \quad (3.8)$$

where

$$\Phi = \Psi C, \quad (3.9)$$

and

$$\begin{aligned}\bar{\Phi} &= (\bar{\Phi}_1, \bar{\Phi}_2), \\ \Psi &= ({}^3\Psi, {}^4\Psi).\end{aligned}$$

Eq. (3.8) and the requirement that $\bar{\Phi}_1$ and $\bar{\Phi}_2$ be normalized implies

$$C = \begin{pmatrix} \cos \theta & \cos \theta \\ \sin \theta & -\sin \theta \end{pmatrix}$$

As R increases without limit, θ approaches

$$\theta_0 = \arctan[(1+S_0^2)/(1-S_0^2)]^{1/2} \text{ and } \bar{\Phi}_1 \text{ approaches } \phi_1^{(0)}$$

Exact primitive functions have been discussed previously by Herring,²² Hirschfelder and Silbey,²¹ and Musher.⁴⁴ Intuitively one expects $\bar{\Phi}_1$ to have electron 1 localized about atom a and electron 2 about atom b. Herring, who calls $\bar{\Phi}_1$ the "home base" function, enforces this intuition by asserting a set of auxiliary conditions that $\bar{\Phi}_1$ must satisfy, such as the requirement that $\bar{\Phi}_1$ approach $\phi_1^{(0)}$ when $r_{a1}=0$ or $r_{b2}=0$. (It is not obvious that this condition can be satisfied.) By contrast, Hirschfelder and Silbey enforce their intuition only in zeroth order by setting up a perturbation sequence for $\bar{\Phi}_1$ which starts from $\phi_1^{(0)}$. This is the approach followed here.

The set of coupled equations satisfied by $\bar{\Phi}$ is

$$H\bar{\Phi} = \bar{\Phi} \mathcal{E}, \quad (3.10)$$

where

$$\mathbb{C} = \mathbb{C}^{-1} \mathbb{E} \mathbb{C}$$

and

$$\mathbb{E} = \begin{pmatrix} {}^q E & 0 \\ 0 & {}^u E \end{pmatrix}$$

It is convenient to define two energies, the Coulomb energy

$$E(\text{coul}) = \frac{1}{2} ({}^q E + {}^u E),$$

and the exchange energy

$$E(\text{exch}) = \frac{1}{2} ({}^q E - {}^u E).$$

Then,

$$\mathbb{C} = \begin{pmatrix} E(\text{coul}) & E(\text{exch}) \\ E(\text{exch}) & E(\text{coul}) \end{pmatrix}$$

Given Φ_1, Φ_2 , the exact wavefunctions ${}^q \Psi$ ${}^u \Psi$ are obtained by projection

$${}^i \Psi = \frac{A_i \Phi_i}{\langle A_i \Phi_i | A_i \Phi_i \rangle^{1/2}}$$

The energies are given by

$$= \langle {}^i \Psi | H | {}^i \Psi \rangle.$$

Perturbation Expansion. The formalism developed in Chapter Two suggests itself as a means of solving Eq. (3.10). It must be extended somewhat, however, since the previous analysis assumed that all of the unperturbed functions are eigenfunctions of the same hamiltonian. This assumption is no longer valid in exchange perturbation problems.

The zeroth order equations corresponding to Eq. (3.10) are defined to be

$$(H_1^{(0)} - E^{(0)}) \phi_1^{(0)} = 0,$$

and

(3.11)

$$(H_2^{(0)} - E^{(0)}) \phi_2^{(0)} = 0.$$

Corresponding to $\phi_1^{(0)}$ and $\phi_2^{(0)}$ are the perturbations

$$H_1^{(1)} = H - H_1^{(0)},$$

and

$$H_2^{(1)} = H - H_2^{(0)},$$

respectively. The superscripts are used in a loose sense to denote the order of perturbation. As discussed in Chapter One, "order" is not a well defined concept, however, since

$$[H_1^{(1)}, P_{12}] = [P_{12}, H_1^{(0)}] = \left(\frac{1}{r_{a1}} + \frac{1}{r_{b2}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) P_{12}. \quad (3.12)$$

Eq. (3.12) states that a "zeroth order" quantity is equal to a "first order" quantity, so that the apparent order of terms can be arbitrarily shifted.

Nevertheless, Eq. (3.10) can be expanded into different orders in a consistent, though arbitrary, manner by defining

$$\mathcal{E} = \mathcal{E}^{(0)} + \sum_{n=1}^{\infty} \lambda^n \mathcal{E}^{(n)},$$

and

(3.13)

$$\Phi = \Phi^{(0)} + \sum_{n=1}^{\infty} \lambda^n \Phi^{(n)},$$

where λ is a formal ordering parameter whose physical value is zero.

The hamiltonian can be resolved in two ways, either as $H_1 = H_1^{(0)} + \lambda H_1^{(1)}$ or as $H_2 = H_2^{(0)} + \lambda H_2^{(1)}$. Only for $\lambda=1$ does $H_1 = H_2 = H$.

The convention adopted here is that when H acts on Φ_k , it is replaced by H_k , $k=1$ or 2 .

Substituting the expansions (3.13) into Eq. (3.10) and equating the coefficient of each power of λ to zero yields, in addition to Eq. (3.11), for $k=1$ and 2 ,

$$(H_k^{(0)} - \mathcal{E}^{(0)}) \phi_k^{(1)} + H_k^{(1)} \phi_k^{(0)} = \sum_{\ell=1}^2 \phi_{\ell}^{(0)} \mathcal{E}_{\ell k}^{(1)}; \quad (3.14)$$

$$(H_k^{(0)} - \mathcal{E}^{(0)}) \phi_k^{(n)} + H_k^{(1)} \phi_k^{(n-1)} = \sum_{m=1}^n \sum_{\ell=1}^2 \phi_{\ell}^{(n-m)} \mathcal{E}_{\ell k}^{(m)}; \quad n \geq 1.$$

Given the solution of the first N perturbation equations (3.14)

the energy is given by

$$i_E = \frac{\langle A_i \Phi_{i(N)} | H | A_i \Phi_{i(N)} \rangle}{\langle A_i \Phi_{i(N)} | A_i \Phi_{i(N)} \rangle},$$

where

$$\Phi_1^{(N)} = \sum_{n=0}^N \phi_1^{(n)}.$$

The justification for this procedure has been developed in Chapter Two. If χ is any wavefunction which is orthogonal to $\Phi_1^{(N)}$ and $\Phi_2^{(N)}$ then the hamiltonian matrix elements $\langle A_2 \Phi_1^{(N)} | H | A_2 \chi \rangle$ vanish through $O(\lambda^{N+1})$. Hence the addition of χ to the basis $\Phi^{(N)}$ affects the energy only by $O(\lambda^{2N+2})$ terms.

Equivalence to Hirschfelder-Silbey Perturbation Theory. It is easily verified that Eq. (3.10) is identical to the equation solved in the Hirschfelder-Silbey exchange perturbation theory for the interaction of ground state hydrogen atoms. Nevertheless, the solution of first order Eq. (3.14) is discussed in detail below in order (1) to demonstrate that, in analogy with almost degenerate perturbation theory, the off-diagonal elements of \mathcal{E} are not completely fixed by the formalism; and (2) to develop a method of solving Eq. (3.14) which reduces the corresponding equation for many-electron systems to one and two electron equations.

Solution of the First Order Equation. Eq. (3.8) implies that $\phi_2^{(1)} = P_{12} \phi_1^{(1)}$, so that it is sufficient to consider only $k=1$ in Eq. (3.14), which may be written

$$(H_1^{(0)} - \epsilon^{(0)}) \phi_1^{(1)} + H_1^{(1)} \phi_1^{(0)} = E^{(1)}_{(cov)} \phi_1^{(0)} + E^{(1)}_{(exch)} \phi_2^{(0)}. \quad (3.15)$$

Multiplying Eq. (3.15) from the left by $\phi_1^{(0)*}$ and integrating yields

$$V_{00} = E^{(1)}(Coul) + S_{00}^2 E^{(1)}(exch), \quad (3.16)$$

where V_{00} is defined by Eq. (3.7). Thus, in analogy with almost degenerate perturbation theory, the requirement of mathematical consistency gives only one equation to determine the two unknown first-order energies.

In the Hirschfelder-Silbey procedure,²¹ a further relation between $E^{(1)}(Coul)$ and $E^{(1)}(exch)$ is obtained by arbitrarily imposing the requirement that the energy through first order agree with the Heitler-London result, Eq. (3.6). This yields

$$E^{(1)}(Coul) = \frac{V_{00} - S_{00}^2 V_{00}'}{1 - S_{00}^4}, \quad \text{and} \quad (3.17)$$

$$E^{(1)}(exch) = \frac{V_{00}' - S_{00}^2 V_{00}}{1 - S_{00}^4},$$

which clearly satisfy Eq. (3.16).

Another way to fix the unknown constants is by a variational method analogous to that introduced in the almost degenerate perturbation theory (see page 36). It was shown there that such a procedure can be expected to have a small effect upon the energy in a rapidly converging perturbation expansion. Thus, the question of applying the variational procedure to the present case cannot be answered without testing the convergence properties of the formalism with numerical examples. For the present, it is assumed that $E^{(1)}(Coul)$ and $E^{(1)}(exch)$ are fixed by Eq. (3.17).

With the constants in Eq. (3.15) fixed, the $\phi_i^{(1)}$ can be obtained. To this end, it is convenient to separate Eq. (3.15) into a polarization equation

$$(H_i^{(0)} - \epsilon^{(0)}) \hat{\phi}_i^{(1)} + (H_i^{(1)} - V_{00}) \phi_i^{(0)} = 0, \quad (3.18)$$

and an exchange equation

$$(H_i^{(0)} - \epsilon^{(0)}) \omega_i^{(1)} = \phi_2^{(0)} - \int_{00}^2 \phi_i^{(0)}, \quad (3.19)$$

where

$$\phi_i^{(1)} = \hat{\phi}_i^{(1)} + \omega_i^{(1)} E^{(1)}(exch).$$

The polarization equation is the first order equation in the unsymmetrical polarization expansion⁵ of ${}^9\Psi$ or ${}^4\Psi$. For the case of H_2 , it has been solved to high accuracy by variational methods by Hirschfelder and Löwdin⁵⁵ and by Kolos.⁵⁶ The primary effect of $\hat{\phi}_i^{(1)}$ is to introduce correlations between the electrons which give rise to van der Waals interactions. The solution of Eq. (3.18) will not be considered further.

The solution of the exchange equation will be considered in detail. In terms of the orbitals a_0 and b_0 , Eq. (3.19) may be written

$$(\hat{h}_a^{(1)} - e_0 + \hat{h}_b^{(1)} - e_0) \omega_i^{(1)}(1,2) = b_0^{(1)} a_0^{(2)} - \int_{00}^2 a_0^{(1)} b_0^{(2)}. \quad (3.20)$$

Thus, Eq. (3.20) is a coupled, two electron, two center equation.

Introducing the complete set of eigenfunctions of \hat{h}_a and \hat{h}_b ,

$$(\hat{h}_a - e_k) a_k = 0 \quad , \quad (\hat{h}_b - e_k) b_k = 0 ,$$

the solution of Eq. (3.20) is

$$\begin{aligned} \omega_i^{(1)}(1,2) &= \sum_{k \neq 0} \sum_{l \neq 0} \frac{\langle a_k | b_0 \rangle a_k^{(1)} \langle b_l | a_0 \rangle b_l^{(2)}}{e'_k + e'_l} \\ &+ S_{00} \left[\sum_{k \neq 0} \frac{\langle a_k | b_0 \rangle a_k^{(1)}}{e'_k} b_0^{(2)} + \sum_{l \neq 0} a_0^{(1)} \frac{\langle b_l | a_0 \rangle b_l^{(2)}}{e'_l} \right], \end{aligned} \quad (3.21)$$

where $e'_k = e_k - e_0$; $e'_l = e_l - e_0$.

The infinite sums in Eq. (3.21) may be evaluated by a technique which⁴⁵ has been used successfully for the calculation of atomic polarizabilities, van der Waals C_6 coefficients, etc. The first sum in Eq. (3.21) is analogous to dispersion energies in the polarization equation and the last two sums are analogous to induction energies.

The sums for $\alpha > 0$ and $\beta > 0$ may be evaluated using the identity,

$$\frac{1}{\alpha + \beta} = \frac{1}{2\pi} \int_0^\infty \left[\frac{1}{\alpha + iu} + \frac{1}{\alpha - iu} \right] \left[\frac{1}{\beta + iu} + \frac{1}{\beta - iu} \right] du, \quad (3.22)$$

which can be shown to be an application of the residue theorem.

Putting $\alpha = e'_k$, $\beta = e'_l$, substituting Eq. (3.22) into

Eq. (3.21) and interchanging the order of summation and integration yields

$$\begin{aligned} \omega_1^{(1)} = & \frac{1}{2\pi i} \int_0^\infty \left[\sum_{k \neq 0} \frac{\langle a_k | b_0 \rangle}{e'_k + iu} a_k^{(1)} + \sum_{k \neq 0} \frac{\langle a_k | b_0 \rangle}{e'_k - iu} a_k^{(1)} \right] \\ & \times \left[\sum_{l \neq 0} \frac{\langle b_l | a_0 \rangle}{e'_l + iu} b_l^{(2)} + \sum_{l \neq 0} \frac{\langle b_l | a_0 \rangle}{e'_l - iu} b_l^{(2)} \right] du \\ & + S_{00} \left[\sum_{k \neq 0} \frac{\langle a_k | b_0 \rangle}{e'_k} a_k^{(1)} b_0^{(2)} + \sum_{l \neq 0} \frac{\langle b_l | a_0 \rangle}{e'_l} a_0^{(1)} b_l^{(2)} \right], \end{aligned}$$

or

$$\begin{aligned} \omega_1^{(1)} = & \frac{1}{2\pi i} \int_0^\infty \left[\xi_+^a(u) + \xi_-^a(u) \right] \left[\xi_+^b(u) + \xi_-^b(u) \right] du \\ & + S_{00} \left[\xi_0^a(u) b_0^{(2)} + a_0^{(1)} \xi_0^b(u) \right], \end{aligned} \quad (3.23)$$

where

$$(h_a - e_0 + iu) \xi_+^a = b_0 - S_{00} a_0,$$

and

$$(h_b - e_0 + iu) \xi_+^b = a_0 - S_{00} b_0,$$

and $\xi_-^a = (\xi_+^a)^*$, $\xi_-^b = (\xi_+^b)^*$: The ξ_0^a and ξ_0^b are the solutions of Eq. (3.24) for $u=0$ In the application³⁵ of the Hirschfelder-Silbey formalism to H_2^+ the first order exchange function $\omega_1^{(1)}$ is simply ξ_0^a defined by Eq. (3.24).

Thus, it has been shown that $\omega_i^{(u)}$ can be obtained by solving the one electron, two center Eq. (3.24) and performing the quadrature, Eq. (3.23).

Eq. (3.24) is still a coupled two-dimensional partial differential equation, and an exact solution in closed form does not appear possible. Variational approximations to the exact solution may be obtained by finding the extreme points of the functional⁴⁶

$$\begin{aligned} & \langle \tilde{\xi}_- | h_a - e_0 + iu | \tilde{\xi}_+ \rangle \\ & - \langle \tilde{\xi}_- | b_0 - S_{00} a_0 \rangle - \langle b_0 - S_{00} a_0 | \tilde{\xi}_+ \rangle \end{aligned} \quad (3.25)$$

where $\tilde{\xi}_+$, $\tilde{\xi}_- = (\tilde{\xi}_+)^*$ are trial functions.

The insight into the nature of $\omega_i^{(u)}$ is provided by the Unsöld approximation¹⁰ to ξ_+^a . The trial function is

$$\tilde{\xi}_+^a = \frac{b_0 - S_{00} a_0}{\beta + iu} \quad (3.26)$$

where β is a parameter determined from the extreme point of Eq. (3.25). A short calculation reveals

$$\beta = \frac{1 - \langle b_0 | \frac{1}{r_a} | b_0 \rangle}{1 - S_{00}^2} = 1 - \frac{1}{R} + O(e^{-R}). \quad (3.27)$$

Substitution of Eq. (3.27) into Eq. (3.23) and integration gives

$$\begin{aligned} \tilde{\omega}_i^{(1)} = & \frac{1}{2\beta} b_o(1) a_o(2) + \frac{S_{oo}}{2\beta} [a_o(1) a_o(2) + b_o(1) b_o(2)] \\ & - \frac{S_{oo}^2}{2\beta} a_o(1) b_o(2). \end{aligned} \quad (3.28)$$

The first and last terms in $\tilde{\omega}_i^{(1)}$ yield multiples of $A_i \phi_i^{(0)}$ upon symmetrization, so that the primary effect of $\tilde{\omega}_i^{(1)}$ is to introduce ionic terms into the wavefunction.

The approximation corresponding to Eq. (3.28) for the polarization function $\hat{\phi}_i^{(1)}$ is

$$\tilde{\hat{\phi}}_i^{(1)} = [\alpha(x_{a1} x_{b2} + y_{a1} y_{b2}) + \alpha' z_{a1} z_{b2}] a_o(1) b_o(2), \quad (3.29)$$

where x_{a1}, y_{a1}, \dots are the cartesian coordinates of the electrons.

The α and α' are variational parameters which vary as R^{-3}

Eq. (3.29) results from evaluating by the Unsöld method the lead term in the multipole expansion of $\hat{\phi}_i^{(1)}$.

With the approximations Eq. (3.28) and (3.29) for $\phi_i^{(1)}$, the wavefunction through first order is given by

$$\begin{aligned} A_i(\phi_i^{(0)} + \tilde{\phi}_i^{(1)}) = & \left[1 + \frac{(1 - S_{oo}^2) E^{(1)}(exch)}{4\beta} \right] A_i a_o(1) b_o(2) \\ & + A_i [\alpha(x_{a1} x_{b2} + y_{a1} y_{b2}) + \alpha' z_{a1} z_{b2}] a_o(1) b_o(2) \\ & + \frac{S_{oo} E^{(1)}(exch)}{2\beta} A_i (a_o(1) a_o(2) + b_o(1) b_o(2)). \end{aligned} \quad (3.30)$$

Eq. (3.30) has precisely the form of the Hirschfelder-Linnett⁵³ (HL) variational wavefunction. If α , α' and β are fixed by the total variational principle, rather than a first order calculation such as Eq. (3.27), the wavefunction Eq. (3.30) yields the HL energy. With β fixed by Eq. (3.27), however, the coefficient of the ionic term in the wavefunction is too small since $S_{oo} E''(\text{exch})$ varies as $\exp(-3R)$. The HL calculations show that the correct coefficient (γ in their notation) varies as roughly $R \exp(-R)$.

Work is currently in progress to obtain $\omega_i^{(1)}$ accurately. There is reason to believe that polarized ionic states²⁹ occur in $\omega_i^{(1)}$. In Chapter Four, a good variational approximation to the total first order wavefunction $\phi_i^{(1)}$ (denoted there by $3\chi + 4\chi$) is obtained, although the form of the basis set does not make it convenient to separate out $\hat{\phi}_i^{(1)}$ and $\omega_i^{(1)}$. The energies (labelled HS) reported in Chapter Four demonstrate that both good coulomb and good exchange energies can be obtained with the wavefunction $A_i(\phi_i^{(0)} + \phi_i^{(1)})$.

3.2 Extension to Many-electron Systems.

The method of solving the first order perturbation equation developed in the preceding paragraphs may be extended to the case of interactions involving many electrons. To avoid the complications which arise when the eigensolutions of the separated-atom system are unknown, consider the interaction of N ground-state hydrogen atoms. A zeroth order primitive function is

$$\phi_i^{(0)} = a_0(1) b_0(2) \cdots n_0(N).$$

This function is degenerate with $N! - 1$ other functions

$$P\phi_i^{(0)} = a_0(p_1) b_0(p_2) \dots n_0(p_N),$$

where P is one of the $N!$ permutations of the electron labels.

The first order equation analogous to Eq. (3.14) is

$$(H_i^{(0)} - \epsilon^{(0)})\phi_i^{(1)} + H_i^{(1)}\phi_i^{(0)} = \sum_P P\phi_i^{(0)} \epsilon_P^{(1)}$$

This may be solved by putting

$$\phi_i^{(1)} = \hat{\phi}_i^{(1)} + \sum_{P \neq 1} \omega_P^{(1)} \epsilon_P^{(1)},$$

which yields the polarization equation

$$(H_i^{(0)} - \epsilon^{(0)})\hat{\phi}_i^{(1)} + (H_i^{(1)} - \langle \phi_i^{(0)} | H_i^{(1)} | \phi_i^{(0)} \rangle)\phi_i^{(0)} = 0, \quad (3.31)$$

and the exchange equations

$$(H_i^{(0)} - \epsilon^{(0)})\omega_P^{(1)} = P\phi_i^{(0)} - \langle \phi_i^{(0)} | P\phi_i^{(0)} \rangle \phi_i^{(0)}. \quad (3.32)$$

In these equations

$$H_i^{(0)} = h_{a(1)} + h_{b(2)} + \dots + h_n(N),$$

$$H_i^{(1)} = \left(\frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{R} \right) + \left(\frac{1}{r_{13}} - \frac{1}{r_{a3}} - \frac{1}{r_{b1}} + \frac{1}{R} \right) + \dots,$$

and $\epsilon^{(0)} = Ne_0$.

The solution to the polarization equation (3.31) has the form

$$\hat{\phi}_i^{(1)} = \hat{\phi}_{ab}^{(1,2)} \frac{\phi_i^{(0)}}{a_0^{(1)} b_0^{(2)}} + \hat{\phi}_{ac}^{(1,3)} \frac{\phi_i^{(0)}}{a_0^{(1)} c_0^{(3)}} + \dots,$$

where

$$(\hat{h}_a^{(1)} - e_0 + \hat{h}_b^{(2)} - e_0) \hat{\phi}_{ab}^{(1,2)} + \left(\frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{R} - V_{00} \right) a_0^{(1)} b_0^{(2)} = 0,$$

which is precisely Eq. (3.18). Thus $\hat{\phi}_i^{(1)}$ in the many electron case is obtained by solving a set of two electron equations.

The exchange equation (3.32) is a coupled k -electron equation if P permutes the labels of k electrons. However, the identity for $a_1, a_2, \dots, a_k > 0$,

$$\frac{1}{a_1 + a_2 + \dots + a_k} = \left(\frac{1}{\pi} \right)^k \int_{-\infty}^{\infty} du_1 \dots \int_{-\infty}^{\infty} du_k \frac{a_1 a_2 \dots a_k \delta(u_1 + u_2 + \dots + u_k)}{(a_1^2 + u_1^2)(a_2^2 + u_2^2) \dots (a_k^2 + u_k^2)},$$

permits the reduction of Eq. (3.32) to k one electron equations of the form of Eq. (3.24). This identity follows from Eq. (3.22).

Thus, in the many electron case the first order perturbation equation may be obtained by solving one and two electron equations.

Summary. The extension to exchange perturbation problems of the formalism developed in Chapter Two leads to the Hirschfelder-Silbey perturbation theory if the undetermined elements of \mathbb{C} are chosen to yield the Heitler-London first order energy. The first order wavefunction may be solved as the sum of the first order polarization function, which introduces van der Waals correlations, and an exchange function, which introduces ionic terms. In the many electron case, the first order equation reduces to a set of one and two electron equations.

IV. MODEL EXCHANGE PERTURBATION THEORY CALCULATIONS

In this Chapter four different types of perturbation theories for exchange forces are applied to three model problems:

- 1) the ground and first excited state of the hydrogen molecule at internuclear separations $R = 4, 6, 8 a_0$;
- 2) a double minimum harmonic oscillator model of H_2^+
- 3) the double minimum delta-function model of H_2^+ .

Since much of this Chapter has already appeared in print, the published articles are reproduced here with Addenda where appropriate. The delta-function calculations have not been published previously.

2.1 Interaction of Two Hydrogen Atoms.

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Exchange and Coulomb Energy of H_2 Determined by Various Perturbation Methods*

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Four different types of perturbation theories for the exchange forces between two atoms are applied to the ground and first excited state of the hydrogen molecule at internuclear separations $R=4, 6, 8a_0$. The energy through second order and the expectation value of the Hamiltonian using the wavefunction accurate through first order are calculated to compare the theories. The results for the Hirschfelder-Silbey procedure are satisfactory. The Murrell-Shaw or Musher-Amos results are equally good with the exception of the Hamiltonian expectation values for both states at $R=6$ and $8a_0$, which are bad. The Eissenschitz-London, van der Avoird, or Hirschfelder (HAV) results are good at small separations but at large separations they give a second-order energy which appears to be about one-half the correct dispersion energy. The Rayleigh-Schrödinger treatment using a Sternheimer type of zeroth-order Hamiltonian gave the best energy for the ground state but not very good energy for the excited state. At the separations considered, deviations from the virial theorem are unimportant.

I. INTRODUCTION

In a previous paper,¹ the mathematical problems associated with the development of a satisfactory perturbation theory for the exchange forces between two atoms were discussed. Many formalisms have been

proposed during the past few years and most of them give different results for the second and higher order energies. From the mathematical standpoint, each of these treatments is equally satisfactory. Thus, we ask the question: "Which formalism provides the best second-order energy and the best expectation value of the Hamiltonian using the wavefunction accurate through the first order?" In the present paper, an attempt is made to answer this question on the basis of accurate numerical calculations.

We consider both the ground state ($^1\Sigma_g^+$) and the first excited state ($^2\Sigma_g^+$) of the hydrogen molecule at the internuclear separations $R=4, 6$, and $8a_0$. The energy through the second order and the expectation value of the Hamiltonian corresponding to $\psi(1, \lambda) = \psi_0 + \lambda\psi^{(1)}$ (where the constant λ is either set equal to

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¹ J. O. Hirschfelder, *Chem. Phys. Letters* **1**, 326, 363 (1967).

one or else energy optimized) are calculated using four different types of perturbation treatments (EL-HAV, HS, MS-MA, and RS). A rather large basis set was used together with vibrational principles to determine the first-order wavefunction $\psi^{(1)}$. The accuracy of the calculations was limited by the rounding errors which resulted from the single-precision computational program.

The results, discussed in Sec. IV, are very interesting, but they do not show that any of the four perturbation schemes is outstandingly better than the other three. The Rayleigh-Schrödinger (RS) is best for the ground state but is not very good for the first excited state. The Hirschfelder-Silbey (HS) results are all satisfactory. The Murrell Shaw (MS) or Musher-Amos (MA) energies are equally good, with the exception of the Hamiltonian expectation values for $R=6$ and $8a_0$ where the values are exceptionally bad. At small separations the Eisen-schitz-London, van der Avoird, or Hirschfelder HAV (EL-HAV) energies are comparatively good, but at large separations the EL-HAV second-order energy becomes approximately one-half of the accurate dispersion energy.

The energy of the triplet state, added to or subtracted from the energy of the singlet state, yields the Coulomb or exchange energy, respectively. A surprise to us is that the perturbation procedures give better values of the exchange energy than of the Coulomb energy. To test whether this result is a property of the perturbation expansions or is due to our use of inaccurate approximations to the first-order wavefunctions, we have also computed total energies using the Rayleigh-Ritz variational principle and the same basis sets as were used in the perturbation calculations. These computations show that the perturbation expansions of the Coulomb energy are slowly convergent.

In terms of computational efficiency, none of the perturbation schemes offers any advantage over a standard Rayleigh-Ritz variational calculation of the total energy, especially if it is necessary to use the trial wavefunction $\tilde{\psi}$ to obtain a reliable estimate of the energy. The major portion of computing time is spent in calculating matrix elements. Since the same elements appear in both methods, a more accurate energy can be obtained by varying the total wavefunction than by varying the first-order wavefunction. The matrix elements for the EL-HAV, HS, and MS-MA second-order energy calculation are significantly simpler, however, since the integrands are not symmetrized. Perturbation techniques are useful in diagnosing the defects in approximate wavefunctions, in calculating accurate expectation values of properties other than energy, and in determining upper and lower bounds. Their practical value in determining the energy depends upon our ability to determine sufficiently accurate solutions to the perturbation equations without recourse to the use of large basis sets.

II. PERTURBATION FORMALISMS USED IN THIS PAPER

The oldest perturbation theory which yields an expansion of the exact wavefunction in terms of symmetrized products of atomic orbitals is that of Eisen-schitz and London (EL).² More modern theories which have the same first-order wavefunction and second-order energy have been developed by van der Avoird³ and by Hirschfelder⁴ (HAV). We also consider the recent perturbation formalisms of Hirschfelder and Silbey (HS),⁴ Murrell and Shaw (MS),⁵ and Musher and Amos (MA),⁶ as well as the usual Rayleigh-Schrödinger (RS) procedure using a Sternheimer-type zeroth-order Hamiltonian.^{7,8} The MS and MA formalisms are equivalent⁹ so that we are dealing with four independent perturbation procedures.

The general structures of the various theories have been fully treated elsewhere.²⁻⁶ Here we simply introduce a notation that is suitable for treating the lowest $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H₂. The exact energy and wavefunction are denoted by iE and $^i\psi$, respectively, with $i=g$ for the gerade state and $i=u$ for the ungerade state. The functions $^g\psi$ and $^u\psi$ are eigenfunctions of the projectors

$$A_g = \frac{1}{2}(1+I)(1+P_{12}), \quad (1a)$$

$$A_u = \frac{1}{2}(1-I)(1-P_{12}), \quad (1b)$$

where P_{12} permutes the electronic coordinates and I inverts the wavefunction through the midpoint of the internuclear axis.

The unperturbed Hamiltonian is defined to be

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - r_{a1}^{-1} - r_{b2}^{-1}, \quad (2)$$

with eigensolutions (e_k, ϕ_k) . The functions ϕ_k are thus products of hydrogen atom wavefunctions. The perturbation V is

$$V = R^{-1} + r_{12}^{-1} - r_{a1}^{-1} - r_{b2}^{-1}. \quad (3)$$

The exact energy and wavefunction are resolved into perturbation series:

$$^iE = E_0 + ^iE^{(1)} + ^iE^{(2)} + \dots, \quad (4)$$

$$^i\psi = A_i\phi_0 + ^i\psi^{(1)} + \dots. \quad (5)$$

² R. Eisen-schitz and F. London, Z. Physik 60, 491 (1930); A. van der Avoird, Chem. Phys. Letters 1, 24 (1967).

³ A. van der Avoird, J. Chem. Phys. 47, 3649 (1967); Chem. Phys. Letters 1, 411 (1967).

⁴ J. O. Hirschfelder and R. Silbey, J. Chem. Phys. 45, 2188 (1966).

⁵ J. N. Murrell and G. Shaw, J. Chem. Phys. 46, 1768 (1967).

⁶ J. I. Musher and A. T. Amos (Preprint); A. T. Amos and J. I. Musher, Chem. Phys. Letters 1, 119 (1967).

⁷ R. M. Sternheimer, Phys. Rev. 96, 951 (1954).

⁸ J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advan. Quant. Chem. 1, 255 (1964).

⁹ R. E. Johnson and S. T. Epstein, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-265, 3 November 1967.

TABLE I. Definition of the operator T_i appearing in Eq. (7).

| Formalism | T_i |
|-----------|---|
| EL-HAV | $A_i(V - {}^iE^{(0)})$ |
| HS | $A_i(V - {}^iE^{(0)}) + A_i(V - {}^uE^{(0)})$ |
| MS-MA | V |

Since our present calculations are limited to iE through the second order and expectation values of the Hamiltonian for ${}^i\psi_0 + {}^u\psi^{(1)}$, we do not need to determine the wavefunction beyond the first order.

The zeroth- and first-order energies are given by the same expressions in all theories considered:

$$\epsilon_0 = -1; \quad {}^iE^{(0)} = \langle \phi_0 | V A_i \phi_0 \rangle / \langle \phi_0 | A_i \phi_0 \rangle. \quad (6)$$

It is in expressions for the second-order energy that we encounter differences. The most direct way to compare the EL-HAV, HS, and MS-MA results is to employ the spectral expansion of ${}^iE^{(2)}$, which may be written

$${}^iE^{(2)} = \langle \phi_0 | A_i \phi_0 \rangle^{-1} \sum_{k \neq 0} \frac{\langle A_i(V - {}^iE^{(0)}) \phi_0 | \phi_k \rangle \langle \phi_k | T_i \phi_0 \rangle}{\epsilon_0 - \epsilon_k}. \quad (7)$$

Here T_i is an operator which depends on the formalism considered. The explicit expressions for T_i are given in Table I.

Because of the form of ${}^iE^{(2)}$, we find it advantageous to define a function

$${}^i\chi = \sum_{k \neq 0} [\langle A_i(V - {}^iE^{(0)}) \phi_0 | \phi_k \rangle^* / (\epsilon_0 - \epsilon_k)] \phi_k. \quad (8)$$

Note that ${}^i\chi$ depends upon the symmetry of the state considered through the projector A_i , although ${}^i\chi$ itself has no simple symmetry properties. The second-order energy in each formalism may be obtained by a single integration involving ${}^i\chi$. That is,

$${}^iE^{(2)} = \langle {}^i\chi | T_i \phi_0 \rangle / \langle \phi_0 | A_i \phi_0 \rangle. \quad (9)$$

The function ${}^i\chi$ is related in a simple way to the first-order wavefunction in the various formalisms.

For the Eisenschitz-London or HAV scheme,¹⁻³

$${}^i\psi^{(1)}(\text{EL-HAV}) = A_i {}^i\chi - (\langle \phi_0 | A_i {}^i\chi \rangle / \langle \phi_0 | A_i \phi_0 \rangle) A_i \phi_0. \quad (10)$$

The second term on the right in (10) assures the orthogonality of ${}^i\psi^{(1)}$ (EL-HAV) to $A_i \phi_0$, which is the normalization condition of van der Avoird³ and Hirschfelder.¹

In the Hirschfelder-Silbey expansion,⁴ ${}^i\psi^{(1)}$ is obtained by projecting a function of the proper symmetry from the sum ${}^u\chi + {}^i\chi$:

$${}^i\psi^{(1)}(\text{HS}) = A_i ({}^u\chi + {}^i\chi). \quad (11)$$

Finally, the Murrell-Shaw⁵ and Musher-Amos⁶

first-order wavefunction is ${}^i\chi$ itself,

$${}^i\psi^{(1)}(\text{MS-MA}) = {}^i\chi. \quad (12)$$

Note that this formalism has the unique feature that the first-order wavefunction does not possess proper symmetry.

The contribution of continuum states makes the sum (8) difficult to evaluate. We shall therefore resort to a variational principle for ${}^i\chi$. It follows from (8) that ${}^i\chi$ satisfies the differential equation

$$(H_0 - \epsilon_0) {}^i\chi + A_i(V - {}^iE^{(0)}) \phi_0 = 0. \quad (13)$$

Since we are considering the states which arise from the ground state of H_0 , the Eq. (13) is equivalent to the variational principle $\delta J = 0$, where

$$J = \langle {}^i\chi | (H_0 - \epsilon_0) {}^i\chi \rangle + \langle {}^i\chi | A_i(V - {}^iE^{(0)}) \phi_0 \rangle + \langle \phi_0 | (V - {}^iE^{(0)}) A_i {}^i\chi \rangle, \quad (14)$$

and ${}^i\chi$ is a trial solution of (13). Note that J does not depend on the component of ϕ_0 in ${}^i\chi$. We use this freedom to satisfy the normalization condition $\langle {}^i\chi | \phi_0 \rangle = 0$.

We choose the trial function ${}^i\chi$ to have the form

$${}^i\chi = \sum_j {}^iC_j \chi_j, \quad (15)$$

$$\chi_j = \exp[-\frac{1}{2}R] (\xi_1 + \xi_2 + \eta_2 - \eta_2) [\xi_1^2 \eta_1^2 \xi_2^2 \eta_2^2 \rho^2], \quad (16)$$

where ξ and η are the usual elliptic coordinates ($\xi = (r_a + r_b)/R$ and $\eta = (r_a - r_b)/R$); $\rho = 2r_{12}/R$, where r_{12} denotes the interelectronic distance; r, s, \bar{r}, \bar{s} are integers in the range 0-4; and $\mu = 0, 1, 2$. The linear coefficients iC_j are variational parameters, and we have taken $N = 30, 50, 70$ for $R = 8, 6, 4a_0$, respectively.

For one- and two-electron systems where the wavefunction is a product of a space function times a spin function, it is possible to use standard Rayleigh-Schrödinger perturbation theory in which a Sternheimer type of zeroth-order Hamiltonian H_{0i} , corresponding to the zeroth-order wavefunction $A_i \phi_0$, is employed. Here

$$H_{0i} A_i \phi_0 = \epsilon_0 A_i \phi_0 \quad \text{and} \quad [H_{0i}, A_i] = 0. \quad (17)$$

The perturbation is then

$$V_i = H - H_{0i}. \quad (18)$$

The Sternheimer Hamiltonian is the only Hamiltonian which satisfies Eq. (17) and can be written as the sum $H_{0i} = K + U_{0i}$, where K is the kinetic energy operator and U_{0i} is a local potential energy function. Jansen¹⁰ and Corinaldesi¹¹ have developed Rayleigh-Schrödinger-type treatments which might be applied to many-electron systems but their zeroth-order Hamiltonians are non-Hermitian and involve nonlocal poten-

¹⁰ I. Jansen, *Phys. Rev.* **162**, 63 (1967).

¹¹ E. Corinaldesi, *Nuovo Cimento* **25**, 1190 (1962); **30**, 105 (1963); E. Corinaldesi and H. E. Lin, *ibid.* **28**, 105 (1963).

tials. The Sternheimer potential energy function is $U_0 = \epsilon_0 - (K A, \phi_0) / (A, \phi_0)$. If now we remember that $H_0 \phi_0 = \epsilon_0 \phi_0$, that $H_0 = K + U_0$, and that K commutes with A_i , it follows that

$$H_0 = K + (A_i U_0 \phi_0) / (A_i \phi_0). \quad (19)$$

Then using our previous notation, $V = U - U_0$, and remembering that U commutes with A_i , it follows that

$$V_i = U - (A_i U_0 \phi_0) / (A_i \phi_0) = (A_i V \phi_0) / (A_i \phi_0). \quad (20)$$

Following the usual Rayleigh-Schrödinger procedure, the equation for $\psi^{(1)}$ (RS) is

$$(H_0 - \epsilon_0) \psi^{(1)}(\text{RS}) + (V_i - {}^iE^{(1)}) A_i \phi_0 = 0, \quad (21)$$

where ${}^iE^{(1)}$ is given by Eq. (6). Because of Eq. (20), we may also write Eq. (21) in the form

$$((H_0 - \epsilon_0) + \{[A_i, U_0] \phi_0 / A_i \phi_0\}) \psi^{(1)}(\text{RS}) + A_i (V - {}^iE^{(1)}) \phi_0 = 0. \quad (22)$$

Equation (22) may be compared with Eq. (13). Again making use of Eq. (20), the Rayleigh-Schrödinger second-order energy is

$${}^iE^{(2)}(\text{RS}) = \langle A_i (V - {}^iE^{(1)}) \phi_0 | \psi^{(1)}(\text{RS}) \rangle / \langle \phi_0 | A_i \phi_0 \rangle. \quad (23)$$

Of course we cannot solve Eq. (21) exactly, but we can use the Hylleraas variational principle^{12,8} to determine an upper bound for the second-order energy ${}^iE^{(2)}$ (RS) and an approximation to the first-order wavefunction $\psi^{(1)}$ (RS). By virtue of Eq. (20), the Hylleraas principle can be written

$$\begin{aligned} & {}^i\tilde{E}^{(2)}(\text{RS}) \langle \phi_0 | A_i \phi_0 \rangle \\ &= \langle \tilde{\psi}^{(1)}(\text{RS}) | (H_0 - \epsilon_0) \tilde{\psi}^{(1)}(\text{RS}) \rangle \\ &+ \langle \tilde{\psi}^{(1)}(\text{RS}) | A_i (V - {}^iE^{(1)}) \phi_0 \rangle \\ &+ \langle A_i (V - {}^iE^{(1)}) \phi_0 | \tilde{\psi}^{(1)}(\text{RS}) \rangle. \quad (24) \end{aligned}$$

By varying $\tilde{\psi}^{(1)}(\text{RS})$ to make ${}^i\tilde{E}^{(2)}(\text{RS})$ a minimum we obtain the best approximation to $\psi^{(1)}(\text{RS})$ and the best approximation ${}^iE^{(2)}(\text{RS})$. Since H_0 and V_i commute with A_i , we can choose the trial function to have the form

$$\tilde{\psi}^{(1)}(\text{RS}) = \sum_j C_j A_i \chi_j, \quad (25)$$

where the χ_j are defined by Eq. (16) and the $s_j + \bar{s}_j$ are restricted to be even integers. Because our trial function varies linearly with the variational parameters C_j , it is easy to show that for the optimum values of C_j the ${}^i\tilde{E}^{(2)}(\text{RS})$ of Eq. (24) is equal to the second-order energy of Eq. (23) if the exact $\psi^{(1)}(\text{RS})$ is replaced by $\tilde{\psi}^{(1)}(\text{RS})$. In our calculations the number

of basis functions used was $N=50, 35$, and 20 for $R=4, 6$, and $8a_0$, respectively.

Thus, for all four types of perturbation procedures which we discuss, the first-order wavefunctions are expressed as linear combinations of the χ_j . The substitution of Eq. (15) into Eq. (14), or Eq. (25) into Eq. (24), together with the variation of the C_j leads in the usual way to a set of simultaneous inhomogeneous linear equations. The solution of these equations is hampered by the near linear dependencies in the set (16) when the expansions (15) or (25) contain a large number of terms. Since the calculations were done in single precision, round-off errors became significant before convergence to the true solutions of (13) and (21) was obtained. At large values of R , accurate values of the integrals were difficult to calculate. Nevertheless, it is believed that the second-order energies obtained possess at least two significant figures (which is sufficiently accurate for our purposes). The calculations were made on the University of Chicago Computing Center IBM 7094 Computer.

Having obtained the approximate first-order wavefunctions $\tilde{\psi}^{(1)}$, it is useful to construct a trial function for the total Hamiltonian $H_0 + V$ of the form

$$\tilde{\psi}(1, \lambda) = A_i \phi_0 + \lambda \tilde{\psi}^{(1)}, \quad (26a)$$

where λ is a variational parameter. The expectation value of the Hamiltonian corresponding to $\tilde{\psi}$,

$${}^i\tilde{E}(1, \lambda) = \langle \tilde{\psi}(1, \lambda) | H^i \tilde{\psi}(1, \lambda) \rangle / \langle \tilde{\psi}(1, \lambda) | \tilde{\psi}(1, \lambda) \rangle, \quad (26b)$$

should then give the energy accurate through the first order of the perturbation and give an upper bound to the true energy of the system.

III. PREVIOUS PERTURBATION CALCULATIONS FOR H_2

In previous papers by Liu, Lyon, and Goodisman¹²; and Matcha and Byers Brown,¹³ the wavefunction and energy for the ground state of the hydrogen molecule have been calculated by perturbation procedures. However, in this previous work the zeroth-order wavefunction was *not* taken to be the symmetrized product of the separated atom wavefunctions and therefore the mathematical problems were quite different from those which we encounter. Liu, Lyon, and Byers Brown¹³ and Goodisman¹² take $\psi_0 = \exp[-c(\xi_1 + \xi_2)]$ and consider the range from $R=1.35a_0$ – $1.45a_0$. Matcha and Byers Brown¹³ take the zeroth-order wavefunction to be the product of the ground-state wavefunction for $11s^+$ for each electron and consider the range from $R=0$ – $2.2a_0$. With a five-

¹² B. Liu, W. D. Lyon, and W. Byers Brown, J. Chem. Phys. **44**, 562 (1966).

¹³ J. Goodisman, J. Chem. Phys. **47**, 1256 (1967).

¹⁴ E. A. Hylleraas, Z. Physik **48**, 469 (1928); *ibid.* **65**, 209 (1930); also, "The Variational Principle in Quantum Mechanics," Rept. No. 1, Inst. Theoret. Phys., University of Oslo, 1961.

¹⁵ R. L. Matcha and W. Byers Brown, J. Chem. Phys. **48**, 74 (1968).

TABLE II. Dissociation results of Matcha and Byers Brown (Ref. 15).

| <i>n</i> | Errors in $D-D_n$ | |
|----------|-------------------|------------------------|
| 1 | +2.7509 eV | 22189 cm ⁻¹ |
| 2 | -0.2683 | -2164 |
| 3 | +0.0293 | 236 |
| 4 | +0.0041 | 33 |
| 5 | +0.0011 | 9 |

term basis set (with optimum scaling) Liu, Lyon, and Byers Brown¹³ determined the energy through second order at the equilibrium separation which corresponded to an energy of dissociation equal to 4.988 eV = 40233 cm⁻¹ or 105% of the experimental value; whereas this same basis set gives a Rayleigh-Ritz variational energy corresponding to 95% of the experimental value. Goodman¹⁴ used a 10-term function to calculate the energy through the third order to obtain a dissociation energy equal to 4.617 eV = 37 241 cm⁻¹ or 97.2% of the experimental. Matcha and Byers Brown¹⁵ used a 50-term basis set and calculated the energy at $R=1.4a_0$ through the fifth order. The accurate Kolos and Wolniewicz¹⁶ variational calculation for the dissociation energy $D = E(\infty) - E = 4.7474$ eV = 38 293 cm⁻¹. If D_n is equal to $E(\infty)$ minus the Rayleigh-Schrödinger perturbation energy calculated through the n th order, then Matcha and Byers Brown¹⁵ obtained the results shown in Table II. Thus, it appears that the Rayleigh-Schrödinger perturbation sequence converges very rapidly under conditions where the zeroth-order wavefunction has the same symmetry as the perturbed wavefunction.

IV. DISCUSSION OF RESULTS

The results of our calculations are given in Tables III-XIII. Let us examine separately each of the tables.

The first two tables show how the second-order energies of the ground state and the first excited state vary with the size of the basis set. In the remaining tables, the numbers quoted correspond to the largest values of N listed.

Tables V and VI compare the accurately calculated variational energies,¹⁶ E , with $\langle E \rangle = \langle \psi^0 | E | \psi^0 \rangle + \langle E^{(2)} |$ and $\langle E^{(1)}, \lambda \rangle$ as determined from the various perturbation procedures. We note the following. (We classify an energy as "good" if it is within ~10% of the accurate energy.)

Ground-state energy through second order. RS is very good, and gives the best energy at $4a_0$. HS and MS-MA are both good and give virtually the same values. These schemes give the best results at 6 and $8a_0$. EL-HAV is fair at $4a_0$, but is bad at $8a_0$. Examination of Table III shows that this is due to $\langle E^{(2)} |$ (EL-HAV) being equal to approximately one-half of the second-order energy of the other schemes at $8a_0$. This is discussed in detail below.

Expectation value of the Hamiltonian for the ground state. RS is good at 4 and $6a_0$, but poor at $8a_0$. The energy is almost unchanged when λ is varied since the optimum λ is nearly unity. HS is quite good at all separations. The optimum λ is nearly unity. MS-MA is almost as good as HS at $4a_0$, but is bad at 6 and $8a_0$. Again, λ is nearly unity. EL-HAV with $\lambda=1$ gives values between those of HS and MS-MA. Variations of λ give considerable improvement in the energy, especially at $8a_0$ where the optimum λ is almost 2. This is related to the behavior of the second-order energy.

Excited state energy through second order. RS is not good at any separation. This is a result of the perturbation V_n of Eq. (20) being very large due to the node of $A_n \psi_0$.¹⁷ HS and MS-MA again give virtually the same results, which range from bad at $4a_0$ to very good at $8a_0$. EL-HAV is bad at all separations. We again note the factor of $\frac{1}{2}$ in the second-order energy at $8a_0$.

Expectation value of the Hamiltonian for the excited state. RS is poor at all separations and not improved by variations in λ . HS is fair at all separations. The optimum λ is nearly unity. MS-MA ranges from fair at $4a_0$ to bad at large separations. Variations of λ fail to improve the energy. EL-HAV exhibits behavior parallel to that in the ground state.

Tables VII and VIII compare the accurate^{16,18} Coulomb energy, $E_{\text{Coul}} = \frac{1}{2}(\langle E \rangle + \langle E \rangle)$, and the exchange energy, $E_{\text{exch}} = \frac{1}{2}(\langle E \rangle - \langle E \rangle)$, with the results of the various perturbation schemes. The exchange energy is very good in all of the methods, especially the Rayleigh-Schrödinger. Surprisingly, the Coulomb energy (which is essentially dispersion energy) is much less accurate for all of the treatments.

It is possible that the poor results for Coulomb energy are a consequence of the limited size of the basis set used to compute the second-order energies, rather than of slowly convergent perturbation expansions. Thus, we have computed the *total* energy of the ground and excited states using the Rayleigh-Ritz variational principle and the *same* basis sets as were used in the perturbation calculations. The results are given in Table IX and show that very accurate values of the Coulomb and exchange energies may be obtained if total energies are computed with the basis sets listed in Tables X and XI. Thus we believe that our computed second-order energies are similarly accurate. Note that using the same basis set as in the perturbation calculations, at $R=8a_0$ we calculated the Rayleigh-Ritz variational energy $\epsilon_0 - \langle E \rangle = 11.74$ cm⁻¹ which is 0.15 cm⁻¹ better than the best previous energy as determined by Kolos and Wolniewicz.¹⁶

Tables X and XI give the coefficients $\langle C_i |$ for the wavefunctions χ and $\psi^{(0)}$ (RS), respectively.

¹⁷ We wish to thank Professor S. T. Epstein for stressing this point to us.

¹⁸ T. O. Hirschfelder and W. J. Meath, *Advan. Chem. Phys.* **12**, 66 (1967).

¹⁹ W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663 (1964).

EXCHANGE AND COULOMB ENERGY OF H_2 TABLE III. $-^2E^{(2)}$ (in atomic units) as a function of N , the number of terms in the basis set.

| R | N | | | | | | | |
|---|--------|-----------|-----------|-----------|------------|-----------|-----------|-----------|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | |
| 4 | EL-HAV | 0.0014217 | 0.0024212 | 0.0027206 | 0.0028814 | 0.0029628 | 0.0030960 | 0.0031377 |
| | HS | 0.0018221 | 0.0028701 | 0.0030362 | 0.0030805 | 0.0030831 | 0.0031350 | 0.0031898 |
| | MS-MA | 0.0018903 | 0.0029819 | 0.0031994 | 0.0032347 | 0.0032586 | 0.0033050 | 0.0033533 |
| | RS | 0.0026307 | 0.0034559 | 0.0036736 | 0.0037517 | 0.0037975 | | |
| 6 | EL-HAV | 0.0000784 | 0.0001459 | 0.0001577 | 0.0001700 | 0.0001897 | | |
| | HS | 0.0001459 | 0.0002465 | 0.0002585 | 0.0002673 | 0.0002797 | | |
| | MS-MA | 0.0001459 | 0.0002466 | 0.0002589 | 0.0002676 | 0.0002803 | | |
| | RS | 0.0001811 | 0.0002510 | 0.0002782 | 0.0002784* | | | |
| 8 | EL-HAV | 0.0000062 | 0.0000159 | 0.0000181 | | | | |
| | HS | 0.0000121 | 0.0000312 | 0.0000350 | | | | |
| | MS-MA | 0.0000121 | 0.0000312 | 0.0000350 | | | | |
| | RS | 0.0000272 | 0.0000334 | | | | | |

* Obtained with 35 terms.

TABLE IV. $-^4E^{(2)}$ (in atomic units) as a function of N , the number of terms in the basis set.

| | | N | | | | | | |
|---|--------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| R | | 10 | 20 | 30 | 40 | 50 | 60 | 70 |
| 4 | EL-HAV | 0.0005320 | 0.0007929 | 0.0009977 | 0.0011131 | 0.0012329 | 0.0013658 | 0.0013952 |
| | HS | 0.0009621 | 0.0012752 | 0.0013367 | 0.0013271 | 0.0013622 | 0.0014077 | 0.0014511 |
| | MS-MA | 0.0009553 | 0.0012682 | 0.0013161 | 0.0013036 | 0.0013113 | 0.0013467 | 0.0013775 |
| | RS | 0.0010077 | 0.0011602 | 0.0012020 | 0.0012091 | 0.0012483 | | |
| 6 | EL-HAV | 0.0000650 | 0.0000867 | 0.0000907 | 0.0000927 | 0.0000973 | | |
| | HS | 0.0001328 | 0.0001877 | 0.0001920 | 0.0001905 | 0.0001877 | | |
| | MS-MA | 0.0001328 | 0.0001878 | 0.0001922 | 0.0001906 | 0.0001878 | | |
| | RS | 0.0001432 | 0.0001684 | 0.0001753 | 0.0001785 | | | |
| | EL-HAV | 0.0000057 | 0.0000148 | 0.0000161 | | | | |
| | HS | 0.0000116 | 0.0000301 | 0.0000331 | | | | |
| | MS-MA | 0.0000116 | 0.0000300 | 0.0000330 | | | | |
| | RS | 0.0000263 | 0.0000312 | | | | | |

* Obtained with 35 terms.

TABLE V. Comparison of perturbation energies with accurate variational energies, (in cm^{-1}). $^1\Sigma_g^+$ ground state, H_2^+

| R | Exact | | | | | |
|-------------------------|--------------------|--------------------------------|--------|--------|--------|--------|
| | $\epsilon_0 - ^2E$ | $\epsilon_0 + ^2E^{(2)} - ^2E$ | EL-HAV | HS | MS-MA | RS |
| $^2E^{(2)} - ^2E$ | | | | | | |
| 4 | 3592.6 | 1115.7 | 427.0 | 415.6 | 379.7 | 282.2 |
| 6 | 178.9 | 67.1 | 25.46 | 5.70 | 5.58 | 5.99 |
| 8 | 11.6 | 7.8 | 3.78 | 0.06 | 0.06 | 0.37 |
| $^2E(1, 1) - ^2E$ | | | | | | |
| 4 | 3592.6 | 1115.7 | 243.8 | 301.8 | 338.5 | 168.4 |
| 6 | 178.9 | 67.1 | 13.93 | 7.56 | 27.13 | 7.51 |
| 8 | 11.6 | 7.8 | 1.87 | 0.14 | 3.88 | 1.36 |
| $^2E(1, \lambda) - ^2E$ | | | | | | |
| 4 | 3592.6 | 1115.7 | 177.8 | 278.1 | 323.5 | 151.1 |
| | | | (1.36) | (1.20) | (1.16) | (1.16) |
| 6 | 178.9 | 67.1 | 9.41 | 7.51 | 27.07 | 7.48 |
| | | | (1.39) | (0.97) | (0.96) | (0.98) |
| 8 | 11.6 | 7.9 | 0.12 | 0.14 | 3.88 | 1.29 |
| | | | (1.92) | (0.99) | (0.97) | (0.90) |

* Here 2E is the accurate variationally calculated energy (Ref. 16); $^2E^{(2)}$ is the energy calculated through the second order of perturbation; $^2E(1, 1)$ is the expectation values of the Hamiltonian calculated with the wavefunction through the first order taking $\lambda=1$ [see Eq. (26)]; and $^2E(1, \lambda)$ is the same as $^2E(1, 1)$ except that λ is optimized to make $^2E(1, \lambda)$ a minimum. The values of λ are given in parentheses.

TABLE VI. Comparison of perturbation energies with accurate variational energies, (in cm^{-1}). $^2\Sigma_u^+$ excited state, H_2^+

| R | Exact | | EL-IIAV | HS | MS-MA | RS |
|---|----------------------|------------------------------------|----------------|-----------------|-----------------------------|-----------------|
| | $\epsilon_0 - {}^uE$ | $\epsilon_0 + {}^uE^{(0)} - {}^uE$ | | | | |
| | | | | | ${}^uE^{(0)} - {}^uE$ | |
| 4 | -1453.3 | 475.8 | 169.6 | 157.3 | 173.4 | 201.4 |
| 6 | -41.2 | 44.8 | 23.47 | 3.62 | 3.61 | 5.66 |
| 8 | 4.3 | 7.3 | 3.77 | 0.05 | 0.06 | 0.42 |
| | | | | | ${}^uE(1, 1) - {}^uE$ | |
| 4 | -1453.3 | 475.8 | 78.1 | 131.3 | 145.7 | 219.7 |
| 6 | -41.2 | 44.8 | 13.40 | 4.35 | 23.69 | 6.87 |
| 8 | 4.3 | 7.3 | 2.01 | 0.31 | 3.87 | 1.01 |
| | | | | | ${}^uE(1, \lambda) - {}^uE$ | |
| 4 | -1453.3 | 475.8 | 39.6 (1.42) | 129.4 (1.08) | 143.6 (1.09) | 218.7 (0.94) |
| 6 | -41.2 | 44.8 | 4.41 (1.89) | 4.33 (0.98) | 23.69 (0.99) | 6.85 (0.97) |
| 8 | 4.3 | 7.3 | 0.29 (1.98) | 0.30 (0.96) | 3.86 (0.97) | 0.99 (0.94) |

* Here uE is the accurate variationally calculated energy (Ref. 16); ${}^uE^{(0)}$ is the energy calculated through the second order of perturbation; ${}^uE(1, 1)$ is the expectation value of the Hamiltonian calculated with the

wavefunction through the first order taking $\lambda=1$ (see Eq. (26)); and ${}^uE(1, \lambda)$ is the same as ${}^uE(1, 1)$ except that λ is optimized to make ${}^uE(1, \lambda)$ a minimum. The values of λ are given in parentheses.

Table XII gives the expectation values of the kinetic energy K for the EL-HAV and HS schemes using the trial wavefunction $\psi(1, \lambda)$ of Eq. (26a) with the optimum value of λ . This permits the determination of a scaling constant s for the approximate wavefunction so that the virial theorem is satisfied. However, as can be seen from Table XIII, even at $4a_0$, the values of s are so near to unity that the improvement in ${}^uE(1, \lambda)$ is very small. At larger separations, the improvements are negligible. The algebra involved in this scaling process is discussed in the Appendix.

Finally, we consider the behavior of ${}^uE^{(2)}$ (EL-HAV) noted above. From Tables III and IV, we see that at $8a_0$,

| | $- {}^uE^{(2)}$ | $- {}^uE^{(2)}$ |
|--------|-----------------------|-----------------------|
| EL-HAV | 3.97 cm^{-1} | 3.53 cm^{-1} |
| HS | 7.68 | 7.26 |
| MS-MA | 7.68 | 7.24 |
| RS | 7.33 | 6.85. |

At $R=8a_0$, the accurate value of the second-order dispersion energy^{16,18} (not considering the exchange of

TABLE VII. Comparison of perturbation Coulomb energies with accurate variational Coulomb energies (in cm^{-1}).*

| R | Exact | | EL-HAV | HS | MS-MA | RS |
|---|--------------------------------|--|--------|-------|---|-------|
| | $\epsilon_0 - E_{\text{Coul}}$ | $\epsilon_0 + E_{\text{Coul}}^{(0)} - E_{\text{Coul}}$ | | | | |
| | | | | | $E_{\text{Coul}}^{(2)} - E_{\text{Coul}}$ | |
| 4 | 1069.6 | 796.1 | 298.3 | 286.4 | 276.6 | 242.0 |
| 6 | 68.8 | 55.9 | 24.47 | 4.66 | 4.60 | 5.83 |
| 8 | 8.0 | 7.6 | 3.78 | 0.06 | 0.06 | 0.40 |
| | | | | | $E_{\text{Coul}}(1, 1) - E_{\text{Coul}}$ | |
| 4 | 1069.6 | 796.1 | 160.9 | 216.6 | 242.1 | 194.0 |
| 6 | 68.8 | 55.9 | 13.67 | 5.96 | 25.41 | 7.19 |
| 8 | 8.0 | 7.6 | 1.94 | 0.22 | 3.88 | 1.19 |
| | | | | | $E_{\text{Coul}}(1, \lambda) - E_{\text{Coul}}$ | |
| 4 | 1069.6 | 796.1 | 108.7 | 203.7 | 233.5 | 184.9 |
| 6 | 68.8 | 55.9 | 6.91 | 5.92 | 25.38 | 7.17 |
| 8 | 8.0 | 7.6 | 0.20 | 0.22 | 3.87 | 1.14 |

* Here $E_{\text{Coul}} = \frac{1}{2}({}^uE + {}^uE)$; the Coulombic energy through the second order of perturbation is $E_{\text{Coul}}^{(2)}$; and the Coulombic energy obtained from the expectation values of the Hamiltonian using the wavefunction through

the first order is $E_{\text{Coul}}(1, \lambda)$. The values given are half the sum of the corresponding values in Tables V and VI.

TABLE VIII. Comparison of perturbation exchange energies with accurate variational exchange energies (in cm^{-1}).^a

| Exact | | | | | | |
|--|--------------------|---|--------|-------|-------|-------|
| R | $-E_{\text{exch}}$ | $E_{\text{exch}}^{(0)}-E_{\text{exch}}$ | EL-HAV | HS | MS-MA | RS |
| $\delta E_{\text{exch}}^{(2)}-E_{\text{exch}}$ | | | | | | |
| 4 | 2423.0 | 320.0 | 128.7 | 129.1 | 103.1 | 40.2 |
| 6 | 110.1 | 11.2 | 1.00 | 1.04 | 0.99 | 0.17 |
| 8 | 3.6 | 0.3 | 0.01 | 0.01 | 0.00 | -0.03 |
| $E_{\text{exch}}(1,1)-E_{\text{exch}}$ | | | | | | |
| 4 | 2423.0 | 320.0 | 82.9 | 85.3 | 96.4 | -25.6 |
| 6 | 110.1 | 11.2 | 0.27 | 1.60 | 1.72 | 0.32 |
| 8 | 3.6 | 0.3 | -0.07 | -0.09 | 0.01 | 0.18 |
| $E_{\text{exch}}(1,\lambda)-E_{\text{exch}}$ | | | | | | |
| 4 | 2423.0 | 320.0 | 69.1 | 74.4 | 90.0 | -33.8 |
| 6 | 110.1 | 11.2 | 2.50 | 1.59 | 1.69 | 0.32 |
| 8 | 3.6 | 0.3 | -0.09 | -0.08 | 0.01 | 0.15 |

^a Here $E_{\text{exch}} = \frac{1}{2}(\langle E - \bar{E} \rangle)$; the exchange energy through the second order of perturbation is $E_{\text{exch}}^{(2)}$; and the exchange energy obtained from the expectation values of the Hamiltonian using the wavefunction through

the first order is $E_{\text{exch}}(1, \lambda)$. The values given are half of the difference between the corresponding values given in Tables V and VI.

electrons between the atoms) is -8.0 cm^{-1} . Thus, the values of $\bar{E}^{(2)}$ calculated by the HS, MS-MA, and RS are approximately equal to the dispersion energy $E^{(2)}(\text{dis})$. However the $\bar{E}^{(2)}(\text{EL-HAV})$ is only about half as large. This raises the question as to whether the $\bar{E}^{(2)}(\text{EL-HAV})$ can be expected to approach the correct $E^{(2)}(\text{dis})$ values in the limit of large separations.

Rigorously, the relation between $\bar{E}^{(2)}(\text{EL-HAV})$ and $E^{(2)}(\text{dis})$ for large values of R is not a simple one, as the following arguments demonstrate. We first substitute (1) into (7) to obtain

$$\bar{E}^{(2)}(\text{EL-HAV}) \sim \frac{1}{2} \sum_{k \neq 0} \frac{|\langle \phi_0 | V \phi_k \rangle|^2}{\epsilon_0 - \epsilon_k} + \frac{1}{2} \sum_{k \neq 0} \frac{|\langle \phi_0 | VI \phi_k \rangle|^2}{\epsilon_0 - \epsilon_k}, \quad (27)$$

where the symbol \sim indicates asymptotic equality. The first summation is $\frac{1}{2}E^{(2)}(\text{dis})$. Although each term in the second summation is exponentially decreasing in R , the series may not be.¹⁷ For example,

$$\sum_{n=0}^{\infty} e^{-R} R^n / n! = 1.$$

A. Arguments That $\bar{E}^{(2)}(\text{EL-HAV}) \sim E^{(2)}(\text{dis})$

In their original paper,¹ Eissenschitz and London used the Unsöld approximation to evaluate $\bar{E}^{(2)}(\text{EL-HAV})$. Taking average energies $\Delta\epsilon^{\dagger}$ and $\Delta\epsilon^{\ddagger}$ from the first (direct) and the second (exchange) series, respectively, in (27) and using the relation $I^2 = 1$ and the completeness of the states ϕ_k , we obtain

$$\bar{E}^{(2)}(\text{EL-HAV}) \sim -\frac{1}{2}(\Delta\epsilon^{\dagger-1} + \Delta\epsilon^{\ddagger-1}) \langle \phi_0 | V^2 \phi_0 \rangle. \quad (28)$$

Eissenschitz and London chose $(\Delta\epsilon^{\dagger-1} + \Delta\epsilon^{\ddagger-1})$ so that the coefficient of R^{-6} in (28) equals the coefficient of R^{-6} in $E^{(2)}(\text{dis})$. In this way they obtained the result, $\frac{1}{2}(\Delta\epsilon^{\dagger-1} + \Delta\epsilon^{\ddagger-1}) = (0.925)^{-1}$. This result appears plausible since the average excitation energy must be greater than 0.75, the energy required to excite the two hydrogen atoms from the $1s$ to the $2s$ or $2p$ states. In this way it would appear that at sufficiently large values of R , so that only the R^{-6} term makes appreciable contributions to the second-order energy, the $\bar{E}^{(2)}(\text{EL-HAV})$ becomes approximately equal to the $E^{(2)}(\text{dis})$.

Van der Avoird¹⁹ has calculated for H_2^+ the values of $\bar{E}^{(2)}$ and $\bar{E}(1, 1)$ using his method (which is equivalent to the EL-HAV scheme) for $R \leq 7a_0$ and obtains excellent agreement with the exact values. However, for H_2^+ at $R=7$ the exchange energy is still large so that he obtains

$$\bar{E}^{(2)} = -252 \text{ cm}^{-1}, \quad \bar{E}^{(2)} = -79 \text{ cm}^{-1}.$$

For this separation Dalgarno and Lynn²⁰ obtained the

TABLE IX. Comparison of the Rayleigh-Ritz variational energies (in cm^{-1}).^a

| R | $\sigma E^{\dagger} - \sigma E$ | $\bar{E}^{\dagger} - \bar{E}$ | $E_{\text{Coul}}^{\dagger} - E_{\text{Coul}}$ | $E_{\text{exch}}^{\dagger} - E_{\text{exch}}$ |
|---|---------------------------------|-------------------------------|---|---|
| 4 | 14.1 | 9.6 | 11.8 | 2.2 |
| 6 | 1.3 | 2.7 | 2.0 | -0.7 |
| 8 | -0.1 | 0.0 | 0.0 | 0.0 |

^a Here σE , \bar{E} , E_{Coul} , E_{exch} are the accurate variational energies (Ref. 16); σE^{\dagger} , \bar{E}^{\dagger} , $E_{\text{Coul}}^{\dagger}$, $E_{\text{exch}}^{\dagger}$ are the variational energies obtained with the same basis sets as were used in the EL-HAV, HS, and MS-MA perturbation calculations.

¹⁹ A. van der Avoird, Chem. Phys. Letters 1, 429 (1967).

²⁰ A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) 70, 223 (1957).

TABLE X. The coefficients C_j for the wavefunction ψ .

| μ | r | s | τ | δ | ξc | | | ηc | | |
|-------|-----|-----|--------|----------|------------|-------------|-------------|-------------|------------|-------------|
| | | | | | $R=4$ | $R=6$ | $R=8$ | $R=4$ | $R=6$ | $R=8$ |
| 0 | 0 | 0 | 0 | 0 | -0.051793 | -0.013709 | -0.071657 | 0.15228 | 0.10664 | -0.063921 |
| 1 | 0 | 0 | 0 | 0 | 0.45177 | 0.43402 | 0.18830 | 0.0069818 | 0.12027 | 0.15467 |
| 0 | 1 | 0 | 1 | 0 | -0.11001 | -0.031741 | -0.43256 | 0.099046 | -0.018047 | -0.037959 |
| 1 | 0 | 1 | 0 | 1 | -0.35631 | -0.67385 | | 0.60628 | 0.20964 | |
| 0 | 0 | 1 | 1 | 0 | -0.16695 | -0.23975 | | 0.26337 | 0.11657 | |
| 0 | 0 | 0 | 1 | 1 | 0.091648 | 0.11947 | | -0.34809 | -0.21667 | |
| 0 | 0 | 0 | 1 | 0 | -0.11157 | -0.24252 | -0.032870 | -0.12545 | -0.068830 | -0.024074 |
| 0 | 1 | 0 | 0 | 0 | -0.084751 | -0.16727 | | -0.11369 | 0.065128 | |
| 0 | 0 | 1 | 0 | 1 | 1.0504 | 1.1978 | | -0.95234 | -0.64999 | -0.17513 |
| 0 | 0 | 0 | 0 | 2 | 0.028365 | -0.04032 | 0.057268 | 0.31171 | 0.082430 | 0.040280 |
| 0 | 1 | 1 | 0 | 0 | -0.33335 | -0.13367 | -0.093795 | -0.33512 | -0.25195 | -0.066610 |
| 0 | 0 | 2 | 0 | 1 | 0.60210 | 0.62991 | -0.18095 | -0.55453 | -0.22399 | -0.14659 |
| 0 | 0 | 1 | 0 | 2 | -0.57767 | -0.60717 | 0.23027 | 0.55846 | 0.17938 | 0.17494 |
| 0 | 0 | 0 | 1 | 1 | 0.14224 | 0.38298 | 0.052554 | 0.35375 | 0.17420 | 0.042859 |
| 1 | 0 | 1 | 0 | 0 | 0.59150 | 0.63977 | 0.18317 | -0.25092 | 0.037367 | 0.14738 |
| 1 | 0 | 0 | 0 | 1 | -0.63361 | -0.62502 | -0.17661 | 0.23356 | -0.020123 | -0.14436 |
| 0 | 0 | 1 | 0 | 0 | -0.23905 | -0.28296 | | 0.33933 | 0.31067 | |
| 0 | 0 | 2 | 0 | 0 | -0.08539 | -0.08783 | | 0.29472 | 0.15259 | |
| 0 | 0 | 2 | 1 | 0 | -0.14806 | -0.10394 | 0.028112 | 0.30545 | 0.12946 | 0.17588 |
| 0 | 1 | 0 | 0 | 2 | -0.18076 | -0.039101 | 0.014502 | 0.29755 | 0.14846 | 0.0072865 |
| 0 | 0 | 1 | 1 | 1 | -0.14124 | 0.03938 | | 0.075088 | 0.10264 | |
| 0 | 0 | 3 | 0 | 0 | 0.052181 | 0.14873 | 0.0059048 | 0.25660 | 0.010843 | 0.00040308 |
| 0 | 0 | 0 | 0 | 3 | -0.082322 | -0.11987 | | -0.26058 | -0.017253 | |
| 0 | 1 | 2 | 0 | 0 | 0.10710 | -0.03649 | | -0.24275 | -0.11048 | |
| 0 | 0 | 0 | 1 | 2 | -0.014495 | 0.11473 | | -0.25695 | -0.069458 | |
| 1 | 0 | 2 | 0 | 0 | 0.24485 | 0.39467 | 0.061095 | -0.19842 | -0.027291 | 0.060231 |
| 1 | 1 | 0 | 0 | 1 | 0.015407 | -0.030071 | 0.018071 | 0.038845 | 0.035779 | 0.010151 |
| 1 | 0 | 1 | 1 | 0 | 0.012253 | -0.064061 | 0.0092641 | -0.020150 | -0.037781 | 0.0072177 |
| 1 | 0 | 0 | 0 | 2 | 0.28491 | 0.34072 | 0.019744 | -0.19044 | 0.016595 | 0.033411 |
| 1 | 1 | 0 | 1 | 0 | 0.014895 | 0.026726 | | 0.011230 | -0.014249 | |
| 0 | 0 | 0 | 0 | 3 | 0.015919 | 0.023200 | | 0.0010312 | -0.0000181 | |
| 0 | 0 | 0 | 2 | 1 | -0.059994 | -0.039295 | | -0.00020925 | 0.0020093 | |
| 0 | 1 | 0 | 0 | 1 | 0.23606 | 0.19028 | | -0.26170 | -0.16341 | |
| 0 | 1 | 0 | 1 | 1 | 0.12773 | -0.014177 | | 0.14794 | 0.017456 | |
| 0 | 0 | 1 | 2 | 0 | 0.011025 | 0.035926 | | -0.036119 | -0.0093768 | |
| 0 | 2 | 0 | 1 | 0 | -0.029322 | -0.00052429 | | -0.010982 | -0.0037828 | |
| 0 | 2 | 0 | 0 | 1 | -0.035706 | -0.012967 | | 0.029166 | 0.020917 | |
| 0 | 1 | 1 | 0 | 1 | -0.094705 | -0.14723 | 0.068493 | 0.077427 | 0.16682 | 0.043811 |
| 0 | 1 | 1 | 1 | 1 | 0.14525 | 0.077035 | | -0.14725 | -0.034027 | |
| 0 | 0 | 2 | 0 | 2 | -0.18694 | -0.043066 | 0.21009 | 0.35176 | -0.026340 | 0.14416 |
| 0 | 3 | 0 | 0 | 0 | 0.011425 | 0.0053026 | | 0.0010916 | -0.0030360 | |
| 0 | 1 | 2 | 0 | 1 | 0.0026651 | -0.079804 | | 0.011013 | 0.054345 | |
| 1 | 0 | 0 | 2 | 0 | -0.019882 | -0.022990 | | -0.0059394 | -0.0068379 | |
| 1 | 1 | 0 | 0 | 2 | 0.011149 | -0.010324 | | -0.038701 | -0.041927 | |
| 1 | 0 | 1 | 0 | 2 | 0.11888 | 0.36121 | -0.12376 | -0.35296 | -0.11629 | -0.075821 |
| 1 | 2 | 0 | 1 | 0 | 0.0069946 | -0.0037171 | | 0.0013877 | 0.0023460 | |
| 1 | 0 | 2 | 1 | 0 | 0.0080525 | -0.013398 | | -0.038144 | -0.036215 | |
| 1 | 0 | 2 | 0 | 1 | -0.11705 | -0.32618 | 0.086687 | 0.35172 | 0.10579 | 0.054464 |
| 2 | 0 | 1 | 0 | 0 | -0.052368 | 0.049678 | | 0.0067828 | -0.0054071 | |
| 2 | 0 | 1 | 0 | 1 | -0.0023228 | -0.076542 | | -0.047024 | 0.0023889 | |
| 0 | 0 | 0 | 2 | 2 | 0.074855 | | | -0.039671 | | |
| 0 | 0 | 0 | 1 | 3 | -0.070934 | | | 0.19798 | | |
| 0 | 0 | 0 | 1 | 4 | 0.031193 | | | 0.023867 | | |
| 0 | 0 | 1 | 1 | 2 | -0.020887 | | | -0.011937 | | |
| 0 | 1 | 1 | 1 | 0 | -0.14127 | | | 0.14244 | | |
| 0 | 0 | 3 | 0 | 3 | 0.11344 | | | -0.12287 | | |
| 0 | 2 | 2 | 0 | 0 | 0.031675 | | | -0.044026 | | |
| 0 | 1 | 3 | 0 | 0 | 0.092418 | | | -0.19611 | | |
| 0 | 0 | 4 | 0 | 0 | -0.083328 | | | 0.023846 | | |
| 1 | 0 | 0 | 2 | 1 | 0.0048235 | | | 0.0049736 | | |
| 1 | 0 | 0 | 1 | 2 | -0.064391 | | | 0.023862 | | |
| 1 | 0 | 0 | 0 | 3 | -0.039594 | | -0.012946 | -0.00032689 | | -0.013326 |
| 1 | 0 | 1 | 1 | 1 | 0.025114 | | | 0.040709 | | |
| 1 | 1 | 1 | 0 | 1 | 0.0047109 | | | 0.041727 | | |
| 1 | 0 | 2 | 0 | 2 | 0.010608 | | -0.11516 | -0.28168 | | -0.066636 |
| 1 | 2 | 1 | 0 | 0 | 0.0022431 | | | -0.0062230 | | |
| 1 | 1 | 2 | 0 | 0 | -0.040334 | | -0.00085946 | 0.025800 | | -0.00093048 |
| 1 | 0 | 3 | 0 | 0 | 0.038687 | | 0.013830 | 0.000079602 | | 0.015427 |
| 2 | 0 | 0 | 0 | 1 | 0.046280 | | | -0.0099149 | | |
| 2 | 1 | 0 | 0 | 0 | -0.021116 | | | -0.0076620 | | |
| 0 | 2 | 0 | 0 | 0 | | | -0.021504 | | | -0.016327 |
| 1 | 0 | 0 | 0 | 0 | | | 0.0060540 | | | 0.0077624 |
| 1 | 0 | 0 | 1 | 0 | | | 0.0072332 | | | 0.0057015 |

EXCHANGE AND COULOMB ENERGY OF H₂TABLE XI. The coefficients C_j for the wavefunction $\tilde{\psi}^{(0)}$ (RS).

| μ | r | s | f | g | g_c | | | u_c | | |
|-------|-----|-----|-----|-----|------------|-------------|-----------|-------------|------------|-----------|
| | | | | | $R=4$ | $R=6$ | $R=8$ | $R=4$ | $R=6$ | $R=8$ |
| 0 | 0 | 0 | 0 | 0 | 1.0795 | 0.47203 | 0.34950 | 0.46901 | 0.11475 | 0.23760 |
| 0 | 0 | 0 | 1 | 0 | -2.4267 | -1.2169 | -0.89202 | -0.59911 | -0.59469 | -0.64864 |
| 1 | 0 | 0 | 0 | 0 | -0.025480 | 0.50379 | 0.28219 | -0.77282 | 0.39560 | 0.23453 |
| 0 | 0 | 0 | 2 | 0 | 0.50808 | 0.21295 | 0.22413 | -0.50208 | 0.063150 | 0.16355 |
| 0 | 1 | 0 | 0 | 0 | 0.75202 | 0.24268 | 0.12079 | -0.18459 | 0.14579 | 0.067388 |
| 0 | 0 | 1 | 0 | 1 | 0.20340 | 0.71649 | -0.17025 | -0.59061 | 0.18786 | -0.19483 |
| 0 | 0 | 0 | 0 | 2 | -0.87846 | -0.84960 | -0.56734 | -0.70433 | -0.44423 | -0.48116 |
| 2 | 0 | 0 | 0 | 0 | -0.29709 | -0.13494 | -0.083826 | -0.40648 | -0.096717 | -0.057912 |
| 0 | 0 | 0 | 1 | 2 | 0.86379 | 0.76862 | 0.42837 | 0.46724 | 0.69628 | 0.36722 |
| 0 | 1 | 0 | 0 | 2 | 0.1605 | 0.66784 | 0.39023 | 0.59328 | 0.40433 | 0.34132 |
| 0 | 0 | 1 | 1 | 1 | 0.41920 | -0.99775 | 0.36429 | 0.65109 | -0.30486 | 0.34082 |
| 1 | 0 | 1 | 0 | 1 | 0.012357 | 0.50529 | 0.020496 | -0.057532 | 0.27165 | 0.065340 |
| 2 | 0 | 0 | 1 | 0 | 0.014939 | 0.0056430 | 0.027311 | 0.18825 | 0.047829 | 0.019018 |
| 2 | 0 | 1 | 0 | 1 | -0.46478 | -0.22085 | -0.023530 | -0.096753 | -0.075474 | -0.015719 |
| 1 | 0 | 1 | 1 | 2 | 0.012780 | -0.0085408 | -0.12639 | -0.21729 | 0.11233 | -0.11726 |
| 0 | 1 | 0 | 0 | 3 | 0.047405 | -0.022361 | -0.030178 | -0.038742 | -0.0079197 | -0.021086 |
| 0 | 2 | 0 | 0 | 2 | -0.45030 | -0.068766 | -0.14566 | -0.39949 | -0.098338 | -0.16418 |
| 1 | 1 | 0 | 0 | 2 | 0.32757 | 0.071650 | 0.031499 | 0.10156 | 0.13111 | 0.056315 |
| 1 | 0 | 2 | 0 | 2 | -0.60541 | -0.32849 | 0.027198 | 0.00034635 | 0.14522 | 0.034654 |
| 0 | 0 | 1 | 2 | 1 | 0.24711 | 0.43031 | -0.060443 | 0.026398 | 0.11720 | -0.091280 |
| 1 | 0 | 0 | 1 | 0 | 1.3183 | | | 2.4656 | | |
| 0 | 0 | 0 | 3 | 0 | -0.029792 | | | 0.17192 | | |
| 0 | 1 | 0 | 2 | 0 | -0.32184 | | | 0.41337 | | |
| 1 | 0 | 0 | 2 | 0 | -0.25421 | | | -0.62435 | | |
| 1 | 0 | 0 | 2 | 2 | -0.40164 | -0.14295 | | 0.25896 | -0.41729 | |
| 1 | 1 | 0 | 1 | 0 | -0.37739 | -0.028536 | | -0.76601 | -0.073163 | |
| 0 | 0 | 0 | 2 | 2 | -0.076728 | 0.0052492 | | 0.15498 | -0.090497 | |
| 0 | 0 | 0 | 0 | 4 | 0.017466 | | | 0.12185 | | |
| 0 | 1 | 0 | 1 | 2 | -0.70930 | -0.51504 | | -0.43101 | -0.32188 | |
| 0 | 2 | 0 | 2 | 0 | 0.0086381 | -0.040965 | | -0.065316 | -0.022744 | |
| 0 | 0 | 2 | 0 | 2 | 0.78541 | 0.78985 | | 0.094660 | -0.057522 | |
| 0 | 1 | 1 | 1 | 1 | -0.39479 | | | -0.062413 | | |
| 1 | 1 | 0 | 2 | 0 | 0.042381 | 0.068055 | | 0.19837 | 0.039404 | |
| 1 | 0 | 1 | 1 | 1 | 0.59609 | | | 0.042489 | | |
| 2 | 0 | 0 | 2 | 0 | 0.020309 | -0.030833 | | 0.021284 | -0.026549 | |
| 2 | 1 | 0 | 1 | 0 | 0.064036 | | | 0.0091210 | | |
| 0 | 1 | 0 | 0 | 4 | -0.032020 | | | -0.094058 | | |
| 0 | 0 | 1 | 1 | 3 | -0.20691 | 0.064291 | | 0.30592 | 0.31121 | |
| 0 | 0 | 1 | 3 | 1 | -0.087062 | | | -0.039437 | | |
| 0 | 0 | 2 | 3 | 0 | 0.040929 | | | 0.069411 | | |
| 0 | 0 | 2 | 1 | 2 | 0.061907 | | | -0.20895 | | |
| 2 | 1 | 0 | 2 | 0 | -0.014838 | | | -0.012007 | | |
| 2 | 1 | 0 | 0 | 2 | -0.028268 | | | 0.0044078 | | |
| 2 | 0 | 1 | 1 | 1 | 0.10815 | | | 0.045803 | | |
| 0 | 2 | 0 | 2 | 2 | 0.057438 | | | 0.037841 | | |
| 0 | 0 | 2 | 2 | 2 | 0.26402 | | | 0.085560 | | |
| 0 | 1 | 1 | 1 | 3 | -0.094076 | | | -0.32568 | | |
| 0 | 1 | 1 | 3 | 1 | -0.015374 | | | -0.00086511 | | |
| 0 | 1 | 2 | 3 | 0 | 0.0065240 | | | 0.013058 | | |
| 2 | 2 | 0 | 0 | 2 | -0.0015669 | | | -0.0084985 | | |
| 0 | 0 | 0 | 0 | 4 | | -0.028163 | | | -0.0092040 | |
| 0 | 0 | 1 | 0 | 3 | | -0.21286 | | | -0.55014 | |
| 1 | 0 | 0 | 3 | 0 | | 0.05989 | | | 0.025084 | |
| 1 | 0 | 3 | 0 | 3 | | 0.014101 | | | 0.047087 | |
| 2 | 0 | 2 | 0 | 2 | | 0.000080012 | | | -0.018930 | |
| 1 | 1 | 0 | 3 | 0 | | -0.0037390 | | | 0.0010645 | |

TABLE XII. Expectation value of the kinetic energy corresponding to $\psi(1, \lambda)$. Here $\psi(1, \lambda)$ is given by Eq. (26a) and $\langle K(1, \lambda) = \langle \psi(1, \lambda) | K^2 \psi(1, \lambda) \rangle / \langle \psi(1, \lambda) | \psi(1, \lambda) \rangle$.

| R | $\langle K(1, \lambda) \rangle$ | | $\langle K(1, \lambda) \rangle$ | |
|-----|---------------------------------|---------|---------------------------------|--------|
| | EL-HAV | HS | EL-HAV | HS |
| 4 | 0.93973 | 0.95241 | 1.0330 | 1.0368 |
| 6 | 0.99540 | 0.99612 | 1.0036 | 1.0028 |
| 8 | 0.99970 | 0.99970 | 1.0002 | 1.0001 |

TABLE XIII. Scaling parameter s for $\psi(1, \lambda)$ and improvement in $\langle E(1, \lambda) \rangle$ resulting from the satisfaction of the virial theorem, $R=4a_0$.

| | | $\langle E(1, \lambda) \rangle$ | |
|--------------|--------|--|---------------------|
| | | $-\langle E(1, \lambda) \rangle_{\text{scaled}}$ | |
| Σ_e^+ | EL-HAV | 0.995 | 7 cm ⁻¹ |
| | HS | 0.987 | 25 cm ⁻¹ |
| Σ_u^+ | EL-HAV | 1.001 | 0 |
| | HS | 1.000 | 0 |

second-order polarization (or dispersion) energy

$$E^{(2)}(\text{pol}) = -222.61 \text{ cm}^{-1}.$$

Actually, we would not expect a meaningful comparison between the $E^{(2)}$ and the $E^{(2)}(\text{pol})$ for separations smaller than the van der Waals' minimum for the $1\sigma_u$ state which occurs²¹ at $R=12.55a_0$. (For H_2 , the van der Waals minimum for the $^2\Sigma_u^+$ state occurs at $R=7.85a_0$. Thus for H_2^+ much larger separations are required for comparable behavior.) Thus, we hope that van der Avoird will extend his calculations to *much* greater separations.

Our calculations indicate that $E^{(2)}(\text{EL-HAV})$ approaches $\frac{1}{2}E^{(2)}(\text{dis})$, however. We point out that we have evaluated the second-order energy with a truncated basis set and we cannot state with certainty that we have converged to the true value of $E^{(2)}(\text{EL-HAV})$. It may be necessary to use a set of terms in the basis set which has the behavior of continuum wavefunctions. Thus we can only say that it *appears* that the Eisen-schitz-London or HAV second-order energy is asymptotically equal to *one-half* of the second-order dispersion energy.

B. Arguments that $E^{(2)}(\text{EL-HAV}) \sim \frac{1}{2}E^{(2)}(\text{dis})$

In a companion paper²² a model for exchange forces is constructed which consists of a particle moving in the one-dimensional potential

$$U(x) = (8R^2)^{-1}(x-R)^2(x+R)^2.$$

The potential $U(x)$ roughly corresponds to the H_2^+ potential, with the nuclear Coulomb attraction replaced by a harmonic oscillator attraction.

In a manner completely analogous to the molecular case, the application of the various perturbation schemes to the model leads to an expansion for the energy consisting of a power series in R^{-1} plus terms exponentially decreasing in R^2 . In this case the summations in (27) may be carried out exactly and it is found that

$$E^{(2)}(\text{dis}) = -(11/32R^2) - (21/512R^4) + \dots,$$

and

$$E^{(2)}(\text{EL-HAV}) \sim -(11/64R^2) - (141/1024R^4) + \dots$$

Thus the exchange series in (27) is of higher order in R^{-1} than the direct series for this model, so that $E^{(2)}(\text{EL-HAV}) \sim \frac{1}{2}E^{(2)}(\text{dis})$.

APPENDIX: THE VIRIAL THEOREM

If a scaling parameter s is introduced into the trial function $\tilde{\psi}(1, \lambda)$ and optimized, the resulting energy $E(1, \lambda)$ satisfies the virial theorem.^{23,24} The equation which determines s is

$$2s^2K(q) + sV(q) + q(\partial\tilde{E}/\partial q) = 0, \quad (29)$$

where $q = sR$, $K(q)$ and $V(q)$ are the expectation values of the kinetic and potential energy, respectively, computed with $\tilde{\psi}$ for $R=q$, and

$$\tilde{E} = s^2K(q) + sV(q). \quad (30)$$

For simplicity we have deleted the superscript i designating the symmetry of E .

The last term in (29) may be estimated by

$$q(\partial\tilde{E}/\partial q) = [(E - \epsilon_0)/(\tilde{E} - \epsilon_0)]R(dE/dR), \quad (31)$$

where E and $R(dE/dR)$ are accurate variational values.¹⁶ Since s is nearly unity for internuclear distances considered, we can solve Eq. (30) by expanding (29)–(31) in power series in $(1-s)$ through quadratic terms, holding q fixed at $q_0 (= 4, 6 \text{ or } 8a_0)$. This yields the scaled energy at $R=q_0/s$. To obtain the scaled energy at $R=q_0$, we expand this result in a power series in $[R - (q_0/s)]$ through linear terms, assuming that s remains constant over the necessary interval.

We used this procedure to estimate s and the improvement in $E(1, \lambda)$ (λ optimized) at the three internuclear distances considered in this paper. At $R=6, 8a_0$ we obtained $s=1$ for all schemes; i.e., the unscaled energies satisfy the virial theorem. The results for $R=4a_0$ are given in Table XIII. We conclude that the energies $E(1, \lambda)$ are not significantly improved by scaling.

²¹ J. M. Peek, Sandia Corp. Research Rept. SC-RR-65-77 (1965).

²² P. R. Certain, J. Chem. Phys. 49, 35 (1968), following article.

²³ J. O. Hirschfelder and J. F. Kincaid, Phys. Rev. 52, 658 (1937).

²⁴ P. O. Löwdin, J. Mol. Spectry. 3, 46 (1959).

Addendum to "Exchange and Coulomb Energy of H_2 Determined by Various Perturbation Methods".

III. Previous Perturbation Calculations for H_2

Other recent perturbation treatments of H_2 are the single center expansion calculations of Dvořáček and Horák,⁵⁴ who obtained a dissociation energy of 4.207 eV; and the calculation of Kirtmān and Pecius,⁵⁷ which employed the same approach as Matcha and Byers Brown with similar results.

IV. Discussion of Results.

As Herring²² has emphasized, the Heitler-London wavefunction $A_i \phi_0$ for the hydrogen molecule predicts the impossible result that the ${}^3\Sigma_u^+$ energy crosses the ${}^1\Sigma_g^+$ energy at large ($R \approx 50a_0$) internuclear separations. The physical reason for this is easy to understand in terms of electron correlations: the electrons are prevented by the exclusion principle from getting too close to each other in the Heitler-London wavefunction for the triplet state; but the singlet wavefunction gives a small, but finite, probability for the electrons to coalesce. This results in an error in the Heitler-London energy for the singlet state which is greater than the error for the triplet state. At large distances, where the error is greater than the splitting between the levels, a crossing occurs. As Table VIII shows, and as has been found by Alexander and Salem,²⁹ accurate numerical values of $E(\text{exch})$ can be obtained by a second order calculation, even though it is not likely that the perturbation theory (in low order) gives the correct analytical R -dependence of $E(\text{exch})$.

A. Arguments that ${}^2E^{(2)}(EL-HAV) \sim E^{(2)}(dis)$.

Van der Avoird has extended³¹ his calculations to $R = 20 a_0$. At $R = 15 a_0$, he also observes the second order energy being too small by a factor of two, but suggests that it could be due to a lack of continuum functions in his basis set.

B. Arguments that ${}^2E^{(2)}(EL-HAV) \sim \frac{1}{2} E^{(2)}(dis)$.

In Section 4.3, the double minimum delta-function model for H_2^+ is solved exactly for the various schemes. In this case it is found that

$$E^{(2)}(dis) = -e^{-2R} + O(e^{-3R}),$$

and

$${}^2E^{(2)}(EL-HAV) = -\frac{1}{2}e^{-2R} + O(e^{-3R}).$$

Thus, for large distance where e^{-3R} can be neglected,

$${}^2E^{(2)}(EL-HAV) \sim \frac{1}{2} E^{(2)}(dis).$$

Thus, although it has not been proved that the EL-HAV second order energy approaches one-half the second order dispersion energy at large distances, this discrepancy has appeared in every application thus far reported. The possibility of modifying the EL-HAV procedure to remove the discrepancy is considered in Appendix D.

Summary of Exchange Perturbation Calculations for H_2 at Large Separations*

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Abstract

This paper is a summary and appraisal of the recent work of the authors together with Kolos and Wolniewicz which applied four types of perturbation procedures to the calculation of the energy of the ground state and first excited state of the hydrogen molecule at large separations. All of the perturbation techniques gave good values for the exchange energy but less accurate values for the Coulombic energy. The reasons why the second-order Eisenschitz-London (or van der Avoird or Hirschfelder *NAV*) energy approaches one-half of the correct limit at large separations are discussed. There seems to be no uniqueness to the orders in an exchange perturbation problem.

There is considerable interest in the development of perturbation procedures for exchange forces where the molecular wave function and the basis set have different symmetries. Different formalisms give different results for the second- and higher-order energies. The mathematical problems have been discussed elsewhere [1]. A basic difficulty is that the *order* of the perturbation terms is not uniquely defined. Thus, if A is the operator which projects the component with the symmetry of the desired molecular wave function, then A commutes with the molecular Hamiltonian H . However, A does not commute with either the zeroth-order Hamiltonian H_0 or the perturbation $V = H - H_0$. Thus, we have the seeming paradox,

$$(1) \quad \begin{array}{l} AH_0 - H_0A = VA - AV \\ \text{Zeroth order} \quad \text{First order} \end{array}$$

In any conventional perturbation scheme, one would suppose that the left-hand side of this equation is zeroth order and the right-hand side is first order. By the use of (1), the apparent orders of various terms in a perturbation expansion can be

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arbitrarily shifted. How subtle are these shifts in the order may be seen from the following derivation.

Let Q_0 be the zeroth-order wave function and let the set of functions Q_0, Q_1, \dots span the Hilbert space of H . The exact wave function can then be written

$$(2) \quad \Psi = Q_0 + \sum_{j \neq 0} c_j Q_j$$

The Schrödinger equation becomes

$$(3) \quad (H - E)Q_0 + \sum_{j \neq 0} c_j (H - E)Q_j = 0$$

Multiplying (3) by a function χ^* and integrating,

$$(4) \quad E = \frac{\langle \chi | H | Q_0 \rangle}{\langle \chi | Q_0 \rangle} + \sum_{j \neq 0} \frac{\langle \chi | H - E | Q_j \rangle c_j}{\langle \chi | Q_0 \rangle}$$

But multiplying (3) by Q_j^* and integrating gives

$$(5) \quad c_j = - \frac{\langle Q_j | H - E | Q_0 \rangle}{\langle Q_j | H - E | Q_j \rangle} - \sum_{\substack{k \neq j \\ k \neq 0}} \frac{\langle Q_j | H - E | Q_k \rangle c_k}{\langle Q_j | H - E | Q_j \rangle}$$

Substituting (5) into (4), and iterating,

$$(6) \quad E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

where

$$(7) \quad E^{(0)} = \frac{\langle \chi | H_0 | Q_0 \rangle}{\langle \chi | Q_0 \rangle}, \quad E^{(1)} = \frac{\langle \chi | V | Q_0 \rangle}{\langle \chi | Q_0 \rangle}$$

$$E^{(2)} = \sum_{j \neq 0} \frac{\langle \chi | H - E | Q_j \rangle \langle Q_j | H - E | Q_0 \rangle}{\langle \chi | Q_0 \rangle \langle Q_j | H - E | Q_j \rangle}$$

The convergence of the sequence depends upon the non-diagonal elements $\langle Q_j | H - E | Q_k \rangle$ being small compared with the diagonal elements $\langle Q_j | H - E | Q_j \rangle$. If $\chi = Q_0$, (6) is the familiar Brillouin-Wigner series. For the present examples, let $Q_0 = Af_0$ and $Q_j = f_j$ for $j \neq 0$, where

$$(8) \quad (H_0 - \epsilon_0)f_0 = (H_0 - \epsilon_j)f_j = 0$$

The lowest orders of the BL-HAV (Eisenschitz-London [2], van der Avoird [3], or HAV [1]) perturbation procedures correspond to setting $\chi = Q_0 = Af_0$. Then

$$(9) \quad E^{(0)} = \epsilon_0, \quad E^{(1)} = \frac{\langle f_0 | V | Af_0 \rangle}{\langle f_0 | Af_0 \rangle}$$

$$E_{\text{BL-HAV}}^{(2)} = - \sum_{j \neq 0} \frac{\langle f_0 | (V - E^{(1)}) A | f_j \rangle \langle f_j | A (V - E^{(1)}) | f_0 \rangle}{\langle f_0 | Af_0 \rangle (\epsilon_j - \epsilon_0)} + O(V^3)$$

Here $O(V^3)$ are terms which appear to be "third order" or higher in the perturbation. In any case, the $O(V^3)$ terms do not appear in the EL-HAV second-order energy.

The lowest orders of the MS-MA (Murrell-Shaw [4] or Musher-Amos [5]) procedures correspond to setting $\chi = f_0$. In this case, $E^{(0)}$ and $E^{(1)}$ are the same as before, but

$$(10) \quad E_{\text{MS-MA}}^{(2)} = - \sum_{j \neq 0} \frac{\langle f_0 | V | f_j \rangle \langle f_j | A(V - E^{(1)}) | f_0 \rangle}{\langle f_0 | A f_0 \rangle (\epsilon_j - \epsilon_0)} + O'(V^3)$$

Here the $O'(V^3)$ apparent "third order" and higher terms do not appear in the MS-MA second-order energy.

Although the derivation of the $E_{\text{EL-HAV}}^{(2)}$ and the $E_{\text{MS-MA}}^{(2)}$ are very similar, the resulting formulae are quite different. The difference between these two "second-order" energies can be traced to "third-" and higher-order terms in the perturbation sequences.

There have been many other types of perturbation schemes proposed for calculating exchange forces. One of the most curious is the HS (Hirschfelder-Silbey [1, 6]) scheme which proposes that there exists a physically significant "primitive function" whose symmetry projections correspond to the wave functions for the family of quantum states arising from a single-electron configuration. The function f_0 is the zeroth order of the primitive function.

Intuitively, the ideal perturbation treatment would seem to be the straight Rayleigh-Schrödinger (RS) procedure. For one- or two-electron problems where the wave function separates into a space function times a spin function, Sternheimer [7a] showed how to form a satisfactory zeroth-order Hamiltonian. If K is the kinetic energy operator and Af_0 is the zeroth-order wave function, then the "Sternheimer Hamiltonian" is

$$(11) \quad H'_0 = K + \left[\epsilon_0 - \frac{KAf_0}{Af_0} \right]$$

Clearly, $H'_0 Af_0 = \epsilon_0 Af_0$. The Sternheimer Hamiltonian together with Af_0 forms the basis for setting up a Rayleigh-Schrödinger perturbation procedure. The Sternheimer Hamiltonian is the only possible zeroth-order Hamiltonian corresponding to the zeroth-order wave function Af_0 which has a local potential. Unfortunately the Sternheimer Hamiltonian cannot be generalized conveniently to many-electron systems [7b].

Since there is no way of telling *a priori* from the formalism which of the various perturbation schemes gives the *best* second-order energy or gives the *best* expectation value of the Hamiltonian corresponding to the wave function accurate through the "first" order, we must resort to mathematical experimentation. The hydrogen molecule would seem to be the best "guinea pig". Recently, Certain, Hirschfelder, Kolos, and Wolniewicz [8] have made calculations for both the $^1\Sigma_g^+$ ground state

and the $^3\Sigma_u^+$ first excited state using a basis set of Coolidge and James type functions (70, 50, and 30 terms for $R = 4, 6$, and $8a_0$, respectively, for the EL-HAV, HS, and MS-MA procedures; and 50, 35, and 20 terms for $R = 4, 6$, and $8a_0$, respectively, for the RS). The first-order wave functions were determined by varying the coefficients of these basis functions so as to satisfy a variational principle. The zeroth-order wave functions are the usual Heitler-London expressions.

TABLE I. Accurate variationally determined energies of the ground state (g) and the first excited state (u) of the hydrogen molecule. E_{Coul} and E_{exch} are given by (12) and (13).

| R/a_0 | $\epsilon_0 - {}^gE$ | ${}^uE - \epsilon_0$ | $\epsilon_0 - E_{\text{Coul}}$ | $-E_{\text{exch}}$ |
|---------|-------------------------|-------------------------|--------------------------------|-------------------------|
| 4 | 3592.6 cm ⁻¹ | 1453.3 cm ⁻¹ | 1069.6 cm ⁻¹ | 2523.0 cm ⁻¹ |
| 6 | 178.9 | 41.2 | 68.8 | 110.1 |
| 8 | 11.6 ^a | -4.3 | 8.0 | 3.6 |

^a In the new variational calculations given in [8] the improved value of 11.74 cm⁻¹ was obtained.

Table I gives the accurate binding energy of the ground state $^1\Sigma_g^+$ of the hydrogen molecule, $\epsilon_0 - {}^gE$, and the accurate energy of interaction of two hydrogen atoms in the first excited $^3\Sigma_u^+$ state of the hydrogen molecule, ${}^uE - \epsilon_0$. These values were previously determined by Kolos and Wolniewicz [9] using the Rayleigh-Ritz variational principle together with a very large basis set. The corresponding accurate Coulombic and exchange energies are respectively [10],

$$(12) \quad \epsilon_0 - E_{\text{Coul}} = \frac{1}{2}[(\epsilon_0 - {}^gE) - ({}^uE - \epsilon_0)]$$

$$(13) \quad -E_{\text{exch}} = \frac{1}{2}[(\epsilon_0 - {}^gE) + ({}^uE - \epsilon_0)]$$

It should be remembered that $\epsilon_0 - {}^gE = 38293$ cm⁻¹ at the equilibrium separation $R = 1.4a_0$. Also, the minimum in the ${}^uE - \epsilon_0$ occurs at $R = 6.85a_0$.

TABLE II. Contribution of the first-order energies to the interaction, Coulombic and exchange energies.

| R/a_0 | ${}^gE^{(1)}/(\epsilon_0 - {}^gE)$ | ${}^uE^{(1)}/({}^uE - \epsilon_0)$ | $-E_{\text{Coul}}^{(1)}/(\epsilon_0 - E_{\text{Coul}})$ | $-E_{\text{exch}}^{(1)}/-E_{\text{exch}}$ |
|---------|------------------------------------|------------------------------------|---|---|
| 4 | 0.69 | 1.33 | 0.26 | 0.87 |
| 6 | 0.62 | 2.09 | 0.19 | 0.90 |
| 8 | 0.33 | 0.70 | 0.05 | 0.92 |

Table II shows the fraction of the interaction energy which is given by the first-order contribution. Here, in accordance with (9), $\epsilon_0 + {}^gE^{(1)}$ and $\epsilon_0 + {}^uE^{(1)}$ are the expectation values of the Hamiltonian for the molecule using the Heitler-London wave functions for the $^1\Sigma_g^+$ ground state (g) and the $^3\Sigma_u^+$ first excited state (u), respectively. The first-order Coulombic and exchange energies, ${}^gE_{\text{Coul}}^{(1)}$

and $E_{\text{exch}}^{(1)}$ are given by (12) and (13) with the first-order energies replacing the total energies of the system. This definition of Coulombic and exchange energies is slightly different from the one which chemists have used in connection with Heitler-London wave functions. Writing

$$(14) \quad \epsilon_0 + {}^1E^{(1)} = (J \pm L)/(1 \pm S)$$

the chemists have regarded J and L as approximations to the Coulombic and exchange energies. With our definition, the corresponding Coulombic and exchange energies are $(J - SL)/(1 - S^2)$ and $(L - SJ)/(1 - S^2)$, respectively. The two definitions differ since the overlap integral S is not zero. There is a considerable body of evidence from the theories of many-electron systems, the solid state, and ferromagnetism which shows that our definition is the more meaningful [11]. At $R = 4, 6$, and $8a_0$ the value of S is 0.0357, 0.0022, and 0.0001, respectively. Because the value of S is small, our conclusions would not be changed if we had changed our definition of E_{exch} and E_{Coul} .

From Table II it appears that the interaction energy as determined by the first-order energy is, for the ground state, too small and, for the first excited state, too large. The first-order energies give only a small fraction of the Coulombic energy and indeed $-E^{(1)}/(\epsilon_0 - E_{\text{Coul}})$ should approach zero at large separations where the Coulombic energy becomes equivalent to the second-order dispersion energy. It is indeed surprising that E_{exch} gives 90 % of the exchange energy without any appreciable variation with the separation.

Tables IIIa and IV give the results of the Certain, Hirschfelder, Kolos, and Wolniewicz calculations corresponding to various types of perturbation procedures. Let us examine separately each of the subsections of Table III.

(a) *Ground-state energy through second order.*

rs is very good, best at $R = 4a_0$.

HS and MS-MA are both good and give virtually the same values, best at $R = 8a_0$.

EL-HAV is good at $R = 4a_0$, and becomes bad at $R = 8a_0$.

(b) *Excited-state energy through second order.*

rs is not good at any separation.

HS and MS-MA again give virtually the same values, slightly better than rs at $R = 4$ and $6a_0$ but still not good, and very good at $R = 8a_0$.

EL-HAV is the same as HS and MS-MA at $R = 4$, but is very bad at $R = 6$ and $8a_0$.

(c, e, and Table IV) *Expectation value of the Hamiltonian for the ground state wave function through the first order.*

rs is good at $R = 4$ and $6a_0$ but poor at $8a_0$. The energy is almost unchanged when λ is varied since the optimum λ is nearly unity.

TABLE III. The energy through the second-order, ${}^1\epsilon^{(2)}$; the expectation value of the Hamiltonian corresponding to the wave function through the first order, ${}^1E(1, 1)$; the ${}^1E(1, 1)$ improved by optimizing the normalization of the first-order wave function, ${}^1\bar{E}(1, \lambda)$; and the corresponding Coulomb and exchange energies.

| R/a_0 | EL-HAV | HS | MS-MA | RS | EL-HAV | HS | MS-MA | RS |
|--|--------|------|-------|------|--|------|-------|------|
| (a) $(\epsilon_0 - {}^s\epsilon^{(2)})/(\epsilon_0 - {}^sE)$ | | | | | (b) $({}^u\epsilon^{(2)} - \epsilon_0)/({}^uE - \epsilon_0)$ | | | |
| 4 | 0.88 | 0.88 | 0.89 | 0.92 | 1.12 | 1.11 | 1.12 | 1.14 |
| 6 | 0.86 | 0.97 | 0.97 | 0.97 | 1.57 | 1.09 | 1.09 | 1.14 |
| 8 | 0.67 | 0.99 | 0.99 | 0.97 | 0.12 | 0.99 | 0.99 | 0.90 |
| (c) $(\epsilon_0 - {}^sE(1, 1))/(\epsilon_0 - {}^sE)$ | | | | | (d) $({}^uE(1, 1) - \epsilon_0)/({}^uE - \epsilon_0)$ | | | |
| 4 | 0.93 | 0.92 | 0.91 | 0.95 | 1.05 | 1.09 | 1.10 | 1.15 |
| 6 | 0.92 | 0.96 | 0.85 | 0.96 | 1.33 | 1.11 | 1.57 | 1.17 |
| 8 | 0.84 | 0.99 | 0.67 | 0.88 | 0.53 | 0.93 | 0.09 | 0.77 |
| (e) $(\epsilon_0 - {}^sE(1, \lambda))/(\epsilon_0 - {}^sE)$ | | | | | (f) $({}^uE(1, \lambda) - \epsilon_0)/({}^uE - \epsilon_0)$ | | | |
| 4 | 0.95 | 0.92 | 0.91 | 0.96 | 1.03 | 1.09 | 1.10 | 1.15 |
| 6 | 0.95 | 0.96 | 0.85 | 0.96 | 1.11 | 1.11 | 1.57 | 1.17 |
| 8 | 0.99 | 0.99 | 0.67 | 0.89 | 0.93 | 0.93 | 0.10 | 0.77 |
| (g) $(\epsilon_0 - \epsilon_{\text{Coul}}^{(2)})/(\epsilon_0 - E_{\text{Coul}})$ | | | | | (h) $\epsilon_{\text{exch}}/E_{\text{exch}}$ | | | |
| 4 | 0.72 | 0.73 | 0.74 | 0.77 | 0.95 | 0.95 | 0.96 | 0.98 |
| 6 | 0.64 | 0.93 | 0.93 | 0.92 | 0.99 | 0.99 | 0.99 | 1.00 |
| 8 | 0.53 | 0.99 | 0.99 | 0.95 | 1.00 | 1.00 | 1.00 | 1.00 |
| (i) $(\epsilon_0 - E(1, 1)_{\text{Coul}})/(\epsilon_0 - E_{\text{Coul}})$ | | | | | (j) $E(1, 1)_{\text{exch}}/E_{\text{exch}}$ | | | |
| 4 | 0.85 | 0.80 | 0.77 | 0.82 | 0.97 | 0.96 | 0.96 | 1.01 |
| 6 | 0.80 | 0.91 | 0.63 | 0.90 | 1.00 | 0.99 | 0.98 | 1.00 |
| 8 | 0.76 | 0.97 | 0.51 | 0.85 | 1.02 | 1.03 | 1.00 | 0.95 |
| (k) $(\epsilon_0 - E(1, \lambda)_{\text{Coul}})/(\epsilon_0 - E_{\text{Coul}})$ | | | | | (l) $E(1, \lambda)_{\text{exch}}/E_{\text{exch}}$ | | | |
| 4 | 0.90 | 0.81 | 0.78 | 0.83 | 0.97 | 0.97 | 0.96 | 1.02 |
| 6 | 0.90 | 0.91 | 0.63 | 0.90 | 0.98 | 0.99 | 0.98 | 1.00 |
| 8 | 0.97 | 0.97 | 0.53 | 0.86 | 1.03 | 1.02 | 1.00 | 0.96 |

TABLE IV. Optimum value of the parameter λ which optimizes the energy ${}^1E(1, \lambda)$.

| R/a_0 | Ground state | | | | First excited state | | | |
|---------|--------------|------|-------|------|---------------------|------|-------|------|
| | EL-HAV | HS | MS-MA | RS | EL-HAV | HS | MS-MA | RS |
| 4 | 1.36 | 1.20 | 1.16 | 1.16 | 1.42 | 1.08 | 1.09 | 0.94 |
| 6 | 1.39 | 0.97 | 0.96 | 0.98 | 1.89 | 0.98 | 0.99 | 0.97 |
| 8 | 1.92 | 0.99 | 0.97 | 0.90 | 1.98 | 0.96 | 0.97 | 0.94 |

HS is not as good as RS when $R = 4a_0$, equal to $6a_0$ and much better at $8a_0$. Altogether HS is quite good at all separations. The optimum λ is nearly unity so that the energy is not improved by the variation of λ .

MS-MA is almost as good as HS for $R = 4a_0$ but is very bad at 6 and $8a_0$. Again, λ is nearly unity and the energy is not improved by variations of λ .

EL-HAV with $\lambda = 1$ gives values lying approximately half way between HS and MS-MA; it is good at $R = 4a_0$, fair at $6a_0$, and poor at $8a_0$. Variations of λ make a considerable improvement in the energy, especially at $R = 8a_0$ where the optimum value of λ is almost two. The $\lambda = 2$ at large separations corresponds to the second-order energy being one-half of the dispersion energy. For the optimized values of λ , the EL-HAV energies are very good at all separations.

(d, f, and Table IV) *Expectation of the Hamiltonian for the excited state wave function through the first order.*

RS is poor at all separations and not improved by variations in λ since the optimum values of λ are nearly unity.

HS is fair at all separations and not improved by variations in λ since the optimum values of λ are nearly unity.

MS-MA is fair at $R = 4a_0$ but very bad at larger separations. These energies are not improved by variations in λ since the optimum values of λ are nearly unity.

EL-HAV with $\lambda = 1$ gives a good energy at $R = 4a_0$ but bad energy (between HS and MS-MA) at larger separations. Again, the EL-HAV energies are considerably improved by variations of λ . At $R = 6$ and $8a_0$ the optimum value of λ is very nearly equal to two, corresponding to the second-order energy becoming at large separations too small by a factor of one half. With the optimum values of λ , the EL-HAV energies are good.

(g, i, and k) *Coulombic energy.*

RS is poor for $R = 4a_0$ and somewhat better for 6 and $8a_0$. The results for the energy through the second order are somewhat better than is obtained with the expectation values for the Hamiltonian at 6 and $8a_0$.

HS Coulombic energies are comparable to RS at $R = 4$ and $6a_0$, but become good to very good at $8a_0$. Again the energy through the second-order gives better results than the expectation value of the Hamiltonian at 6 and $8a_0$.

MS-MA Coulombic energy through the second order is virtually the same as for the HS; however, the expectation values of the Hamiltonian give much worse results, especially at large separations.

EL-HAV gives very poor Coulombic energy through the second order. With $\lambda = 1$, the expectation values of the Hamiltonian give poor results. However, with the optimum value of λ , the Coulombic energies obtained from the expectation values of the Hamiltonian are good at all separations.

(h, j, and l) *Exchange energy.*

All four perturbation procedures give very good values of the exchange energy at all separations. The values obtained using the energy through the second order are virtually perfect at $R = 6$ and $8a_0$.

Conclusions

We reach four general conclusions.

[1]. *Of all the schemes which we considered, the Hirschfelder-Silbey procedure gives the most uniformly good results.* Nevertheless, we are not enthusiastic about this method because it is difficult to understand the physical significance of the "primitive function" whose projections give the exact wave function for both the singlet (g) and the triplet (u) states. Furthermore, the variational principle for the first-order wave function minimizes

$$\langle f_0 | A_g | f_0 \rangle {}^gE^{(2)} + \langle f_0 | A_u | f_0 \rangle {}^uE^{(2)}$$

rather than ${}^gE^{(2)}$ and ${}^uE^{(2)}$ separately.

[2]. *All of the perturbation procedures give good values for the exchange energy but not as accurate values for the Coulombic energy.* Table II shows that most of the exchange energy is given by the first order but very little of the Coulombic energy is given by the first-order terms. One would expect that the Coulombic energy should agree accurately with the second-order dispersion energy at $R = 8a_0$ and the agreement should still be fairly good at $R = 6$ and $4a_0$. The second-order dispersion energy is

$$(15) \quad E_{\text{disp}}^{(2)} = \sum_{i \neq 0} |\langle f_0 | V | f_i \rangle|^2 / (\epsilon_0 - \epsilon_i)$$

In devising a new type of perturbation scheme for exchange problems, it would be desirable to require that the E_{Coul} be equal to the E_{disp} . One might suppose that the error in E_{Coul} might be due to the basis set which was used rather than in the perturbation methods themselves. However, this notion is dispelled by Table V where it is shown that using the Rayleigh-Ritz variational procedure with

TABLE V. Energies (designated by tilde) determined by Rayleigh-Ritz variational procedure using the same basis set as was used for the RI-C-HAV, HS, and M3-MA perturbations, compared to accurate energies of Table I.

| R/a_0 | $\epsilon_0 - {}^g\tilde{E}$ $\epsilon_0 - {}^gE$ | ${}^u\tilde{E} - \epsilon_0$ ${}^uE - \epsilon_0$ | $\epsilon_0 - \tilde{E}_{\text{Coul}}$ $\epsilon_0 - E_{\text{Coul}}$ | $-\tilde{E}_{\text{exch}}$ $-E_{\text{exch}}$ |
|---------|--|--|--|--|
| 4 | 1.00 | 1.01 | 0.99 | 1.00 |
| 6 | 0.99 | 1.06 | 0.97 | 1.01 |
| 8 | 1.01 | 1.00 | 1.00 | 1.01 |

the same basis sets gives extremely good values of both the Coulombic and exchange energies. Thus, we would get about the same order of accuracy for the energies of the singlet and triplet states if we followed the suggestion of Robinson [12] and took the exchange energy to be $E_{\text{exh}}^{(1)}$ and the Coulombic energy to be $E_{\text{dis}}^{(2)}$. This would have the advantage of greatly simplifying the calculations. Of course, the precision would not be improved.

[3]. At large separations, the second-order EL-HAV energy seems to approach one half the Coulombic (or dispersion) energy. This is seen most clearly in Table VI. All of the

TABLE VI. Comparison of the second-order perturbation energies with the accurate Coulombic energy.

| R/a_0 | $-^sE^{(2)}/(\epsilon_0 - E_{\text{Coul}})$ | | | | $-^uE^{(2)}/(\epsilon_0 - E_{\text{Coul}})$ | | | |
|---------|---|------|-------|------|---|------|-------|------|
| | EL-HAV | HS | MS-MA | RS | EL-HAV | HS | MS-MA | RS |
| 4 | 0.64 | 0.65 | 0.69 | 0.78 | 0.29 | 0.30 | 0.28 | 0.26 |
| 6 | 0.60 | 0.89 | 0.89 | 0.89 | 0.31 | 0.60 | 0.60 | 0.57 |
| 8 | 0.50 | 0.96 | 0.96 | 0.92 | 0.44 | 0.91 | 0.91 | 0.86 |

other perturbation methods gives values of $-^sE^{(2)}$ and $-^uE^{(2)}$ which approach $(\epsilon_0 - E_{\text{Coul}})$ at large separations. Closely related is the fact (as shown in Table IV) that the optimum value of λ for the EL-HAV approaches two at large separations whereas the optimum value of λ for the other perturbation schemes is close to unity. Let us consider more closely the behavior of $E^{(2)}$ (EL-HAV) as given by (9).

For the singlet (g) and the triplet (u) states we have the projection operators $A_g = (1/4)(1 + I)(1 + P_{12})$ and $A_u = (1/4)(1 - I)(1 - P_{12})$ where P_{12} permutes the electronic coordinates and I inverts the wave function through the midpoint of the internuclear axis. The $f_j = a_{\text{HIA}}(1)b_{\text{HIA}}(2)$ is the product of a hydrogen orbital for electron "1" about center "a" times another hydrogen orbital for electron "2" about center "b". We will let f'_j be the function f_j with electrons "1" and "2" interchanged.

At large separations, there are simplifications in (9) which can be made since the second-order energy varies as $1/R^6$ and we can neglect terms which decrease exponentially with the separation. However, we must be careful since an infinite sum of terms, each of which decreases exponentially with R , may vary as a power of $1/R$. Before writing down the asymptotic expression for the second-order energy we should note that the overlap integrals, $\langle f_j | f'_k \rangle$, the first-order energies, $^sE^{(1)}$ and $^uE^{(1)}$, and the second-order exchange energy all decrease exponentially with R . Furthermore, Table III.h assures us that the EL-HAV exchange energy through the second order behaves properly at large separations. Thus, at large separations, to the accuracy which we require, $^sE^{(2)} = ^uE^{(2)} = E_{\text{Coul}}^{(2)}$. Using (9)

to obtain the equation for $E_{\text{Coul}}^{(2)}$ and expressing its limit as R becomes large,

$$(16) \quad E^{(2)}(\text{EL-HAV}) = \frac{1}{2} E_{\text{disp}}^{(2)} - \frac{1}{2} \sum_{j \neq 0} \frac{|\langle f_0 | V | f_j \rangle|^2}{\epsilon_j - \epsilon_0}$$

Each term in the summation decreases exponentially with R . However, without a detailed investigation we cannot reach any firm conclusions about the behavior of the sum. It certainly seems unlikely that at large separations $E^{(2)}(\text{EL-HAV})$ would have the correct limiting form equal to $E_{\text{disp}}^{(2)}$. Our calculations for H_2 indicate that it does not.

Van der Avoird [13a] has calculated for H_2^+ the values of ${}^1E^{(2)}$ and ${}^1E(1, 1)$ using his method (which is equivalent to the EL-HAV scheme). For $R \leq 7a_0$ he obtains excellent agreement with the exact values. For these separations the exchange energy is larger than the Coulombic energy, however, and we would not expect a meaningful comparison between ${}^1E^{(2)}$ and $E_{\text{disp}}^{(2)}$ for separations smaller than the van der Waals minimum for the excited state, which occurs at $12.55a_0$. At our suggestion, van der Avoird [13b] has extended his calculations to distances up to $20a_0$ and finds that for large R , the second term in (16) vanishes with respect to the first. He also finds that highly excited states make a substantial contribution to the sum in (16) for large R , suggesting that accurate values are difficult to obtain with a truncated basis set.

For an analogous double minimum one-dimensional potential, Certain [14] was able to evaluate the corresponding expressions rigorously and in this case he found that the sum in (16) was smaller than $E_{\text{disp}}^{(2)}$ by a factor of the order of R^{-2} .

[4]. *If the perturbation schemes that we have considered are to have practical value in determining energies, new methods must be developed for solving perturbation equations without recourse to the use of large basis sets* [15]. Table III shows quite clearly that third- and higher-order contributions to the energy must be included to obtain accurate results. The effort involved in such a calculation would certainly be greater than a straightforward Rayleigh-Ritz variational calculation if it were necessary to employ large basis sets and variational principles to compute each order of energy.

In the various schemes for perturbations involving electron exchange, for properties other than energy, one still has "Dalgarno-type" interchange theorems. However, the interchanged perturbation equations are themselves extremely difficult to solve.

Further research is required to develop new techniques for solving perturbation equations or to establish a procedure for exchange problems which is more satisfactory than the ones which we have considered.

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4.2 Harmonic Oscillator Model.

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One-Dimensional Model for Exchange Forces*

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Four different types of perturbation theories for the exchange forces between two atoms are applied to the lowest gerade and ungerade state of a simple one-dimensional model. It is shown that the second-order energy in one of the expansions (the Eissenschitz-London, van der Avoird, or Hirschfelder HAV expansion) exhibits undesirable behavior in the limit corresponding to large internuclear distances.

I. INTRODUCTION

The formal¹⁻⁷ and computational⁸⁻¹² aspects of the development of a satisfactory perturbation theory for exchange forces between two atoms have received a great deal of attention recently. In an application¹¹ of three different types of perturbation treatments (EL-HAV, HS, and MS-MA) to the interaction of two hydrogen atoms, it was discovered that the EL-HAV (Eissenschitz-London, van der Avoird, or Hirschfelder HAV) expression for the second-order energy apparently fails to agree with the second-order dispersion energy (no electron exchange) at large internuclear separations, where exchange forces are negligible. No-rigorous statement regarding this discrepancy could be made, however, since the second-order energy was not evaluated exactly.

In the present paper, we apply the following formalisms to lowest gerade and ungerade states of a simple one-dimensional model:

RS: An unsymmetrical Rayleigh-Schrödinger expansion. The second-order energy is analogous to the second-order dispersion energy of the H-H interaction.

EL-HAV: Eissenschitz-London,¹ van der Avoird,⁸ or Hirschfelder HAV⁶ expansion. These expansions give the same expression for the second-order energy.

HS: Hirschfelder-Silbey expansion.²

MS-MA: Murrell-Shaw³ or Musher-Amos⁴ expansion. These two formalisms are equivalent.⁷

This model calculation has the advantage that the

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² J. O. Hirschfelder and R. Silbey, J. Chem. Phys. 45, 2188 (1966).

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⁴ J. I. Musher and A. T. Amos (Preprint); A. T. Amos and J. I. Musher, Chem. Phys. Letters 1, 149 (1967).

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¹¹ P. R. Certain, J. O. Hirschfelder, W. Kolos, and L. Wolniewicz, J. Chem. Phys. 49, 24 (1968), preceding paper.

¹² L. Jansens, Chem. Phys. Letters 1, 417 (1967).

EL-HAV second-order energy can be evaluated exactly. The discrepancy with the analogous "dispersion energy" is verified for this model. The results obtained here are also relevant to the question⁴: "Which formalism provides the *best* second-order energy and the *best* expectation value of the Hamiltonian using the wavefunction accurate through the first order?" As in the application¹¹ to the hydrogen-hydrogen interaction, we do not find any of the four perturbation schemes outstandingly better than the other three.

II. A SIMPLE MODEL FOR EXCHANGE FORCES

We consider the one-dimensional system described by the Schrödinger equation

$$-\frac{1}{2}\psi''(x) + U(x)\psi(x) = E\psi(x), \quad (1)$$

where

$$U(x) = (1/8R^2)(x-R)^2(x+R)^2. \quad (2)$$

The potential $U(x)$ has minima at $x = \pm R$ and a maximum at $x = 0$ of height $R^2/8$. As R increases without limit, $U(x)$ evolves into two simple-harmonic-oscillator (SHO) potentials centered at $\pm R$. Thus, at $R = \infty$ the lowest state is doubly degenerate with $E = \frac{1}{2}$. As R decreases, this state is split into a gerade and an ungerade state under the influence of two physical effects. The first, a long-range effect due to the lowering of the barrier height, increases the space available to a particle in the lowest state and decreases its energy. The gerade-state energy is affected more since symmetry forces the ungerade-state wavefunction to have a small amplitude beneath the barrier. The second effect, a short-range effect due to the decrease in separation between the wells, restricts the particle to a smaller region and increases its energy.

These considerations indicate that the energy of the lowest state decreases initially as R decreases from infinity. This state splits into a g and a u state, with the g state decreasing in energy more rapidly than the u state. Finally, at short range the energy of both states increases to infinity. This is the same qualitative behavior as is found for the lowest states of H_2^+ and H_2 , and is the reason for the choice of the model.

In the discussion which follows, E will denote the *exact* energy of the lowest gerade ($i=g$) and ungerade ($i=u$) state. Although no closed form solution exists for (1), the method of Secrest, Cashion, and Hirsch-

felder¹³ can be used to obtain ϵ to the required accuracy.

III. RAYLEIGH-SCHRÖDINGER EXPANSION

For R large the minimum in $U(x)$ at $x = -R$ is a small perturbation of an SHO potential at $x = R$. To show this we change variables to $q = R - x$. Then (1) becomes

$$(H_0 + V - E)\psi(q) = 0, \quad (3)$$

where

$$H_0 = -\frac{1}{2}(d^2/dq^2) + \frac{1}{2}q^2, \quad (4)$$

$$V = -(1/2R)q^3 + (1/8R^3)q^4. \quad (5)$$

The eigenfunctions of H_0 are $(\phi_k, \epsilon_k = k + \frac{1}{2})$, where

$$\phi_k = (\sqrt{\pi} 2^k k!)^{-1/2} \exp(-q^2/2) H_k(q), \quad (6)$$

and the $H_k(q)$ are Hermite polynomials.

The natural perturbation parameter is R^{-1} . This choice does not correspond to the symmetrical expansions, however, so instead we expand in powers of the total perturbation V . The usual formulas of Rayleigh-Schrödinger perturbation theory¹⁴ yield

$$E^{(0)} = \epsilon_0 = \frac{1}{2},$$

$$E^{(1)}(\text{RS}) = 3/32R^2,$$

$$E^{(2)}(\text{RS}) = -(11/32R^3) - (21/512R^4), \quad (7)$$

and

$$\psi^{(0)}(\text{RS}) = \phi_0,$$

$$\psi^{(1)}(\text{RS}) = \frac{1}{R} \left(\frac{3\sqrt{2}}{8} \phi_1 + \frac{\sqrt{3}}{12} \phi_3 \right) - \frac{1}{R^2} \left(\frac{3\sqrt{2}}{32} \phi_3 + \frac{6\sqrt{2}}{64} \phi_5 \right).$$

This approach does not recognize the inversion symmetry ($x \rightarrow -x$) of the total Hamiltonian and produces a wavefunction which has neither gerade nor ungerade symmetry. A simple way to obtain such a function to act on $\psi^{(0)}(\text{RS}) + \psi^{(1)}(\text{RS})$ with operators which project onto gerade and ungerade function spaces. These operators are

$$A_g = \frac{1}{2}(1 + I), \quad (8)$$

$$A_u = \frac{1}{2}(1 - I),$$

where I is the inversion ($x \rightarrow -x$) operator. In this way we obtain a trial wavefunction

$$\tilde{\psi}(\text{RS}) = A_g \psi^{(0)}(\text{RS}) + \lambda_i A_u \psi^{(1)}(\text{RS}), \quad (9)$$

where λ_i is a variational parameter, and use it to compute the expectation value of the total Hamiltonian $H = H_0 + V$:

$$\tilde{E}(\text{RS}) = \langle \tilde{\psi}(\text{RS}) | H | \tilde{\psi}(\text{RS}) \rangle / \langle \tilde{\psi}(\text{RS}) | \tilde{\psi}(\text{RS}) \rangle. \quad (10)$$

¹³ D. Secrest, K. Cashion, and J. O. Hirschfelder, J. Chem. Phys. 37, 830 (1962).

¹⁴ J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Advan. Quantum Chem. 1, 265 (1964).

It has recently been shown¹⁶ that the resolvent operator for a Hamiltonian which is the sum of the SHO Hamiltonian and a polynomial perturbation $\lambda P(x)$ of degree exceeding two is not expressible in a convergent power series in λ . Thus the energy is not analytic at $\lambda = 0$. This is true even if the total potential $\frac{1}{2}x^2 + \lambda P(x)$ is bounded from below, since in this case the potential $\frac{1}{2}x^2 - \lambda P(x)$ is not bounded. The RS scheme is of this type for the model considered here, and will therefore not converge. Nevertheless, the wavefunction (9) is a valid trial function and (10) yields an upper bound to the true energy.

IV. SYMMETRIZED EXPANSIONS

The general structures of the EL-HAV, HS, and MS-MA formalisms have been fully treated elsewhere.¹⁻⁷ The zeroth- and first-order energies and the zeroth-order wavefunction are the same in all three formalisms:

$$\epsilon^{(0)} = \epsilon_0 = \frac{1}{2},$$

$$\epsilon^{(1)} = \langle \phi_0 | V A_i \phi_0 \rangle / \langle \phi_0 | A_i \phi_0 \rangle = (3/32R^2) \mp \frac{1}{2}[(1 + R^2) \epsilon^{-R^2} / (1 \pm \epsilon^{-R^2})], \quad (11)$$

where the upper (lower) sign corresponds to $i = g(u)$, and

$$\psi^{(0)} = A_i \phi_0. \quad (12)$$

It is in expressions for the second-order energy and first-order wavefunction that we encounter differences. The most direct way to compare the results is with the spectral expansions of $\epsilon^{(2)}$ and $\psi^{(1)}$:

$$\epsilon^{(2)} = \langle \phi_0 | A_i \phi_0 \rangle^{-1} \sum_{k \neq 0} \langle T_i \phi_0 | \phi_k \rangle \langle \phi_k | S_i \phi_0 \rangle / (\epsilon_0 - \epsilon_k), \quad (13)$$

$$\psi^{(1)} = \sum_{k \neq 0} [\langle \phi_k | S_i \phi_0 \rangle / (\epsilon_0 - \epsilon_k)] P_i \phi_k + \alpha_i A_i \phi_0. \quad (14)$$

Here P_i is a symmetry projector, S_i and T_i are operators which differ in the various formalisms, and α_i is a constant which fixes the normalization of $\psi^{(1)}$. Explicit expressions for P_i , S_i , T_i , α_i are given in Table I.

The sums for $\epsilon^{(2)}$ and $\psi^{(1)}$ are easily evaluated numerically. Below we shall consider in detail the analytical evaluation of $\epsilon^{(2)}$ (EL-HAV) for large R . Having obtained $\psi^{(1)}$ we construct the trial wavefunction $\tilde{\psi}$ analogous to (9),

$$\tilde{\psi} = \psi^{(0)} + \lambda_i \psi^{(1)}, \quad (15)$$

and compute the expectation value of H ,

$$\tilde{E} = \langle \tilde{\psi} | H | \tilde{\psi} \rangle / \langle \tilde{\psi} | \tilde{\psi} \rangle, \quad (16)$$

with λ_i optimized.

¹⁶ W. M. Frank, J. Math. Phys. 8, 1121 (1967).

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TABLE I. Definitions of operators and constants appearing in Eqs. (13) and (14).

| Formalism | T_i | S_i | P_i | α_i |
|-----------|------------------------|---|-------|--|
| EL-HAV | $A_i(V - {}^tE^{(0)})$ | $A_i(V - {}^tE^{(0)})$ | A_i | chosen so that $\langle \psi^{(0)} \psi^{(0)} \rangle = 0$ * |
| HS | $A_i(V - {}^tE^{(0)})$ | $A_i(V - {}^tE^{(0)}) + A_u(V - {}^uE^{(0)})$ | A_i | 0 |
| MS-MA | V | $A_i(V - {}^tE^{(0)})$ | 1 | 0 |

* This is the normalization used by van der Avoird⁴ and Hirschfelder.⁵

V. DISCUSSION

Table II contains the exact energies tE , the partial sums of the perturbation energies ${}^tE^{(0)} + {}^tE^{(1)} + {}^tE^{(2)}$, and the expectation value of the Hamiltonian \bar{E} . The results obtained here achieve significance only if it is

expected that analogous features will be observed in molecular calculations. The results of similar calculations¹¹ for the hydrogen molecule reveal striking parallels. Thus there is good reason to believe that conclusions reached here will remain valid for molecular systems.

TABLE II. Energy of the lowest gerade and ungerade states.

| R | tE Exact | A. Gerade | | | | \bar{E} [Eqs. (10), (16)] Optimum λ in parentheses | | | |
|-----|------------------|---|--------|--------|--------|--|--------------------|--------------------|--------------------|
| | | ${}^tE^{(0)} + {}^tE^{(1)} + {}^tE^{(2)}$ | | | | | | | |
| | | RS | EL-HAV | HS | MS-MA | RS | EL-HAV | HS | MS-MA |
| 0.8 | 0.3308 | 0.0093 | 0.1757 | 0.0883 | 0.0273 | 0.3469 (0.2254) | 0.3488 (0.3302) | 0.3529 (0.2391) | 0.3675 (0.2625) |
| 1.0 | 0.2940 | 0.2090 | 0.2083 | 0.1433 | 0.1008 | 0.3082 (0.3042) | 0.3089 (0.4528) | 0.3145 (0.3187) | 0.3305 (0.3427) |
| 1.2 | 0.2806 | 0.3066 | 0.2337 | 0.1812 | 0.1521 | 0.2995 (0.4023) | 0.2967 (0.5964) | 0.3061 (0.4124) | 0.3236 (0.4339) |
| 2.0 | 0.3502 | 0.4349 | 0.4155 | 0.3827 | 0.3815 | 0.4036 (0.7895) | 0.3857 (1.3935) | 0.4065 (0.7868) | 0.4255 (0.8723) |
| 2.6 | 0.4307 | 0.4621 | 0.4780 | 0.4554 | 0.4554 | 0.4652 (0.8229) | 0.4579 (1.6236) | 0.4652 (0.8228) | 0.4808 (0.9184) |
| 3.0 | 0.4604 | 0.4715 | 0.4883 | 0.4707 | 0.4707 | 0.4775 (0.8252) | 0.4751 (1.6077) | 0.4775 (0.8252) | 0.4905 (0.9000) |
| 5.0 | 0.4895 | 0.4899 | 0.4967 | 0.4899 | 0.4899 | 0.4911 (0.9185) | 0.4909 (1.8314) | 0.4911 (0.9185) | 0.4972 (0.9366) |
| R | uE Exact | B. Ungerade | | | | \bar{E} [Eqs. (10), (16)] Optimum λ in parentheses | | | |
| | | ${}^uE^{(0)} + {}^uE^{(1)} + {}^uE^{(2)}$ | | | | | | | |
| | | RS | EL-HAV | HS | MS-MA | RS | EL-HAV | HS | MS-MA |
| 0.8 | 1.1403 | 0.0093 | 0.8999 | 0.6178 | 0.6013 | 1.1764 (0.1849) | 1.1829 (0.3457) | 1.1775 (0.2062) | 1.2132 (0.2744) |
| 1.0 | 0.9314 | 0.2090 | 0.8495 | 0.7023 | 0.7089 | 0.9452 (0.2345) | 0.9485 (0.4523) | 0.9456 (0.2531) | 0.9690 (0.3378) |
| 1.2 | 0.7870 | 0.3066 | 0.7527 | 0.6676 | 0.6652 | 0.7945 (0.2778) | 0.7958 (0.5536) | 0.7945 (0.2914) | 0.8112 (0.3924) |
| 2.0 | 0.5232 | 0.4349 | 0.5257 | 0.4916 | 0.4918 | 0.5255 (0.4895) | 0.5269 (0.9494) | 0.5251 (0.4902) | 0.5390 (0.5850) |
| 2.6 | 0.4776 | 0.4621 | 0.4915 | 0.4688 | 0.4689 | 0.4836 (0.6946) | 0.4832 (1.3268) | 0.4836 (0.6947) | 0.4975 (0.7705) |
| 3.0 | 0.4740 | 0.4715 | 0.4904 | 0.4707 | 0.4707 | 0.4809 (0.7857) | 0.4802 (1.5031) | 0.4809 (0.7857) | 0.4935 (0.8533) |
| 5.0 | 0.4895 | 0.4899 | 0.4967 | 0.4899 | 0.4899 | 0.4911 (0.9185) | 0.4909 (1.8315) | 0.4911 (0.9185) | 0.4972 (0.9366) |

A desirable feature to require of any symmetrized expansion is that it produces an expression for the energy which agrees, order by order, with that given by the RS scheme for R large enough so that terms $O(e^{-R^2})$ may be neglected. The results in Table II show that the EL-HAV expansion fails to meet this requirement.

For R large we may write

$${}^iE^{(2)}(\text{EL-HAV}) \sim \frac{1}{2} \sum_{k=1}^{\infty} \frac{|\langle \phi_0 | V \phi_k \rangle|^2}{\epsilon_0 - \epsilon_k} + \frac{1}{2} \sum_{k=1}^{\infty} \frac{|\langle \phi_0 | (V - {}^iE^{(1)}) I \phi_k \rangle|^2}{\epsilon_0 - \epsilon_k}, \quad (17)$$

where the tilde indicates asymptotic equality. The first summation is $\frac{1}{2} E^{(2)}(\text{RS})$. To evaluate the second, we use the completeness of the states ϕ_k to write

$$\begin{aligned} \sum_{k=1}^{\infty} \frac{|\langle \phi_0 | (V - {}^iE^{(1)}) I \phi_k \rangle|^2}{\epsilon_0 - \epsilon_k} &= \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \langle \phi_0 | (V - {}^iE^{(1)}) \phi_l \rangle \\ &\times \sum_{k=1}^{\infty} \frac{\langle \phi_l | I \phi_k \rangle \langle \phi_k | I \phi_m \rangle}{\epsilon_0 - \epsilon_k} \langle \phi_m | (V - {}^iE^{(1)}) \phi_0 \rangle. \quad (18) \end{aligned}$$

The advantage of this procedure is that $\langle \phi_0 | (V - {}^iE^{(1)}) \phi_l \rangle$ vanishes for $l > 4$. The overlap integrals $\langle \phi_l | I \phi_k \rangle$ are given by the formula

$$\langle \phi_l | I \phi_k \rangle = \sum_{\alpha=0}^{\min(l,k)} (-1)^{\alpha} \binom{l}{\alpha} \binom{k}{\alpha} \alpha! \left[\frac{x^{l+k-2\alpha}}{l!k!} \right]^{1/2} e^{-x/2}, \quad (19)$$

where $\min(l, k)$ is the smaller of l, k , and $x = 2R^2$. Using this expression and $\epsilon_0 - \epsilon_k = -k$, the summation over k in (18) may be evaluated exactly, yielding

$$\begin{aligned} \sum_{k=1}^{\infty} \frac{\langle \phi_l | I \phi_k \rangle \langle \phi_k | I \phi_m \rangle}{\epsilon_0 - \epsilon_k} &= -e^{-x/2} \left(\frac{x^{l+m}}{l!m!} \right)^{1/2} \\ &\times \left[\text{Ei}(x) - \ln x - \gamma - \sum_{\alpha=1}^M \frac{(\alpha-1)!}{x^{\alpha}} \right. \\ &\left. + \sum_{\alpha=1}^l \frac{l!}{\alpha(l-\alpha)! x^{\alpha}} + \sum_{\alpha=1}^m \frac{m!}{\alpha(m-\alpha)! x^{\alpha}} \right], \quad (20) \end{aligned}$$

where $\text{Ei}(x)$ is the exponential integral,¹⁶ $\gamma = 0.57721 \dots$ is Euler's constant, and M is the larger of l, m . The $\text{Ei}(x)$ has the asymptotic expansion¹⁶

$$e^{-x} \text{Ei}(x) \sim \sum_{\alpha=1}^{\infty} \frac{(\alpha-1)!}{x^{\alpha}}, \quad (21)$$

so that

$$\sum_{k=1}^{\infty} \frac{\langle \phi_l | I \phi_k \rangle \langle \phi_k | I \phi_m \rangle}{\epsilon_0 - \epsilon_k} \sim - \left(\frac{x^{l+m}}{l!m!} \right)^{1/2} \frac{M!}{x^{M+1}} + \dots \quad (22)$$

The nonvanishing matrix elements of V in (18) are

$$\begin{aligned} \langle \phi_0 | V \phi_1 \rangle &= \frac{3}{32R^2} \delta_{10} - \frac{3\sqrt{2}}{8R} \delta_{11} + \frac{3(6)^{1/2}}{16R^2} \delta_{12} \\ &\quad - \frac{\sqrt{3}}{4R} \delta_{13} + \frac{6^{1/2}}{16R^2} \delta_{14}, \quad (23) \end{aligned}$$

where δ_{lm} is the Kronecker delta. This leads to

$$\sum_{k=1}^{\infty} \frac{|\langle \phi_0 | (V - {}^iE^{(1)}) I \phi_k \rangle|^2}{\epsilon_0 - \epsilon_k} \sim - \frac{15}{64R^4} + \dots \quad (24)$$

Thus, ${}^iE^{(2)}(\text{EL-HAV})$ has the asymptotic expansion

$${}^iE^{(2)}(\text{EL-HAV}) \sim -(11/64R^2) - (141/1024R^4) + \dots, \quad (25)$$

so that for R sufficiently large so that terms $O(R^{-4})$ may be neglected, ${}^iE^{(2)}(\text{EL-HAV})$ is one-half of $E^{(2)}(\text{RS})$.

Finally, it is noted that none of the perturbation schemes is strikingly better than the other three. In fact these results indicate that perturbation theory may not be a very efficient way of computing the total energy of systems of this type.

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¹⁶ M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, D.C., 1964), pp. 228-231.

¹⁷ See Ref. 6 for a partial list of participants.

4.3 The Delta-Function Model.

In this Section the different formalisms discussed in Section 4.1 are solved to infinite order in the perturbation for the double minimum delta-function model⁴⁹ of the hydrogen molecule ion. The exact Schrödinger equation and the polarization expansion have been considered previously.⁴⁹ This model is of interest because the exact energy can be obtained in all the methods in analytic form. Further, all of the excited eigenfunctions of the "separated atom" problem are continuum functions, so that to the extent that the model is analogous to molecular problems, the role of the continuum in the evaluation of second order energies may be clarified.

The model consists of the one-dimensional Schrödinger equation

$$(H - E)^\pm \Psi = 0, \quad (4.1)$$

where

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + U(x),$$

and

$$U(x) = -\delta(x - \frac{R}{2}) - \delta(x + \frac{R}{2}),$$

where $\delta(x)$ is Dirac's delta function. The model has two bound-state solutions (E^\pm, Ψ^\pm) , where the superscripts indicate symmetry with respect to inversion ($x \rightarrow -x$).

As R increases without limit, E^+ and E^- each tend to $-\frac{1}{2}$. This is analogous to the behavior of the lowest states of H_2^+ . The model differs from H_2^+ , however, in that there are no algebraically

decreasing terms in $\pm E(R)$ and, hence, the ungerade state has no van der Waals minimum.

The following definitions are introduced:

$$\begin{aligned}
 H^{(0)} &= -\frac{1}{2} \frac{d^2}{dx^2} - \delta(x + \frac{R}{2}) ; \\
 \epsilon^{(0)} &= -\frac{1}{2} ; \quad \phi^{(0)} = e^{-|x + R/2|} ; \\
 H^{(1)} &= -\delta(x - R/2) ; \\
 A_{\pm} &= \frac{1}{2} [1 \pm (x \rightarrow -x)] .
 \end{aligned}$$

Further, the Sternheimer hamiltonian⁴⁷ for this model is

$${}^{\pm} H(\lambda) = {}^{\pm} H^{(0)} + \lambda {}^{\pm} H^{(1)} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1 \pm \lambda e^{-R}}{1 \pm e^{-R}} V(x)$$

To solve the various perturbation formalisms to infinite order, it is convenient to introduce an interpolation equation for each formalism. These equations are listed in Table. 4.1. Each contains a parameter λ in such a way that for $\lambda=0$, the interpolation equation reduces to the unperturbed problem; and for $\lambda=1$, the equation is equivalent to the exact Eq. (4.1). The solution of the interpolation equation is expanded in powers of λ to obtain the perturbation energies and wavefunctions.

Exact Interpolation Energies. The solutions Φ to the interpolation equations in the regions $|x| \neq R/2$ are given in Table 4.2 in terms of unknown constants. These constants are fixed by the continuity $[\Phi(\pm R/2 + \epsilon) = \Phi(\pm R/2 - \epsilon), \epsilon \rightarrow 0]$, normalization, and cusp conditions at the singularities. The last are derived by integrating the interpolating equations over the interval $\pm R/2 - \epsilon \leq x \leq \pm R/2 + \epsilon, \epsilon \rightarrow 0$, and are listed in Table 4.3. In all cases, there are precisely enough equations to fix the unknown constants, including E , uniquely.

The result of the above procedure is a transcendental equation for E , as given in Table 4.4.

It is noted that the Sternheimer and Eissenschitz-London-van der Avoird procedures yield identical interpolating energies. This is apparently a peculiarity of the delta-function model, and not a general result.

Given the expression for the exact E , the radius of convergence of an expansion in powers of λ can in principle be determined. Although this has been done for the polarization procedure,^{49,50} the complexity of the equations discourages the extension to other procedures. At any rate, from a practical point of view, interest centers on how well each of the E , accurate through second-order, mimics the exact energy.

Second-order Energies. Iteration of the transcendental equation for exact energy yields the expression

$$\pm E = -\frac{1}{2} \mp \frac{e^{-R} \pm e^{-2R}}{1 \pm (1+R)e^{-R}} - \frac{1}{2} e^{-2R} + O(e^{-3R}).$$

The first term is the zeroth order energy. The second is the Heitler-London first order energy. The third term will be taken to be the correct asymptotic behavior of second order interpolating energies.

Expansion of the transcendental equations for the interpolating energies in powers of λ leads to the results in Table 4.5 for the asymptotic form of the second order energies. The algebra involved in these calculations was checked by solving the first order equations directly, as discussed in Appendix E.

Discussion. It is noted that the second order energy in the Eisenschitz-London-van der Avoird method differs from that in the polarization expansion by a factor of two, as has been found for the models previously discussed. For the delta-function model, however, this difference is necessary to correct the wrong behavior of the second order polarization energy. The correct asymptotic behavior is also obtained by the Hirschfelder-Silbey and Sternheimer procedures, but not by the Murrell-Shaw-Musher-Amos procedure.

TABLE 4.1: Interpolation Equations for the Schrödinger Equation (4.1).

| Procedure | Equation |
|--|---|
| Exact | $(H^{(0)} + H^{(1)} - \pm E) \pm \Psi = 0$ |
| Polarization ⁵ | $(H^{(0)} + \lambda H^{(1)} - E(\lambda)) \Psi(\lambda) = 0$ |
| Eisenschitz-London, ^{8,9} van der Avoird ¹² or Hirschfelder HAV ¹³ EL-HAV | $[H^{(0)} - \epsilon^{(0)} + A_{\pm}(\lambda H^{(1)} - \pm E(\lambda) + \epsilon^{(0)})] \pm \Phi(\lambda) = 0$ $\pm \Psi = A_{\pm} \pm \Phi$ |
| Murrell-Shaw ¹⁸ or Musher-Amos ²⁰ MS-MA ¹⁹ | $(H^{(0)} + \lambda H^{(1)} - \pm E(\lambda)) \pm \Psi(\lambda) = (1-\lambda) [A_{\pm}, H^{(1)}] \phi^{(0)}$ $\langle \pm \Psi(\lambda) A_{\pm} \phi^{(0)} \rangle = \langle \phi^{(0)} A_{\pm} \phi^{(0)} \rangle$ |
| Hirschfelder-Silbey ^{21,13} HS | $(H^{(0)} + \lambda H^{(1)} - \pm E(\lambda) A_{\pm} - E(\lambda) A_{\pm}) \pm \Phi(\lambda) = 0$ $\pm E(\lambda) = \frac{\langle \phi^{(0)} H^{(1)} A_{\pm} \pm \Phi(\lambda) \rangle}{\langle \phi^{(0)} A_{\pm} \pm \Phi(\lambda) \rangle}$ |
| Sternheimer RS | $(\pm H^{(0)} + \lambda \pm H^{(1)} - \pm E(\lambda)) \pm \Psi(\lambda) = 0$ |

TABLE 4.2: Exact Solutions to Interpolating Equations. $\pm E(\lambda) = -\frac{1}{2}\gamma_{\pm}^2$.

| Procedure | $\pm \Psi(\lambda)$ or $\Phi(\lambda)$ | | |
|--------------|--|--|---|
| | $x > +R/2$ | $-R/2 < x < R/2$ | $x < -R/2$ |
| Exact | $\pm \Psi = A e^{-\gamma_{\pm} x}$ | $; B e^{\gamma_{\pm} x} + C e^{-\gamma_{\pm} x}$ | $; e^{-\gamma_{\pm} x }$ |
| Polarization | $\Psi = A e^{-\gamma_{\pm} x}$ | $; B e^{\gamma_{\pm} x} + C e^{-\gamma_{\pm} x}$ | $; e^{-\gamma_{\pm} x }$ |
| EL-HAV | $\pm \Phi = \pm e^{-\gamma_{\pm} x} + A e^{-x}$ | $; \begin{bmatrix} B(e^{\gamma_{\pm} x} \pm e^{-\gamma_{\pm} x}) \\ + C(e^{-x} \pm e^x) \end{bmatrix}$ | $; e^{-\gamma_{\pm} x } \pm A e^{- x }$ |
| MS-MA | $\pm \Psi = A e^{-\gamma_{\pm} x}$ | $; B e^{\gamma_{\pm} x} + C e^{-\gamma_{\pm} x}$ | $; D e^{-\gamma_{\pm} x }$ |
| HS | $\Phi = e^{-\gamma_{+} x} + A e^{-\gamma_{-} x}$ | $; \begin{bmatrix} B(e^{\gamma_{+} x} + e^{-\gamma_{+} x}) \\ + C(e^{\gamma_{-} x} - e^{-\gamma_{-} x}) \end{bmatrix}$ | $; e^{-\gamma_{+} x } - A e^{-\gamma_{-} x }$ |
| RS | $\pm \Psi = A e^{-\gamma_{\pm} x}$ | $; B e^{\gamma_{\pm} x} + C e^{-\gamma_{\pm} x}$ | $; e^{-\gamma_{\pm} x }$ |

TABLE 4.3: Cusp Conditions for Interpolating Equations.*

| Procedure | $x = -a \equiv -R/2$ | $x = a \equiv R/2$ |
|---|--|--|
| Exact | $\Delta^\pm \Psi'(-a) + 2^\pm \Psi(-a) = 0$ | $\Delta^\pm \Psi'(a) + 2^\pm \Psi(a) = 0$ |
| Polarization | $\Delta^\pm \Psi'(-a) + 2^\pm \Psi(-a) = 0$ | $\Delta^\pm \Psi'(a) + 2^\pm \Psi(a) = 0$ |
| EL-HAV | $\Delta^\pm \Phi'(-a) + \lambda^\pm \Phi(-a) = 0$ | $\Delta^\pm \Phi'(a) + 2^\pm \Phi(a) \pm \lambda^\pm \Phi(-a) = 0$ |
| MS-MA | $\Delta^\pm \Psi'(-a) + 2^\pm \Psi(-a) + (\lambda - 1)e^{-R} = 0$ | $\Delta^\pm \Psi'(a) + 2\lambda^\pm \Psi(a) \pm (1 - \lambda) = 0$ |
| HS | $\Delta^\pm \Phi'(-a) + 2^\pm \Phi(-a) = 0$ | $\Delta^\pm \Phi'(a) + 2\lambda^\pm \Phi(a) = 0$ |
| RS | $\Delta^\pm \Psi'(-a) + 2 \left[\frac{1 \pm \lambda e^{-R}}{1 \pm e^{-R}} \right]^\pm \Psi(-a) = 0$ | $\Delta^\pm \Psi'(a) + 2 \left[\frac{1 \pm \lambda e^{-R}}{1 \pm e^{-R}} \right]^\pm \Psi(a) = 0$ |
| * $\Delta f'(x_0) \equiv \lim_{\varepsilon \rightarrow 0} \left[\frac{df}{dx} \Big _{x=x_0+\varepsilon} - \frac{df}{dx} \Big _{x=x_0-\varepsilon} \right]$ | | |

TABLE 4.4: Transcendental Equations for Exact Interpolating Energies. $\pm E(\lambda) = -\frac{1}{2}\gamma_{\pm}^2$.

| Procedure | Equation |
|--------------|---|
| Exact | $\gamma_{\pm} = 1 \pm e^{-\gamma_{\pm} R}$ |
| Polarization | $(\gamma_{\pm} - \lambda)(\gamma_{\pm} - 1) = \lambda e^{-2\gamma_{\pm} R}$ |
| EL-HAV | $\gamma_{\pm} = \frac{(1 \pm \lambda e^{-R})(1 \pm e^{-\gamma_{\pm} R})}{1 \pm e^{-R}}$ |
| MS-MA | $(\gamma_{\pm} - \lambda)(\gamma_{\pm} - 1) = \lambda e^{-2\gamma_{\pm} R} \pm \frac{2e^{-R}}{1 \pm e^{-R}} \left[\frac{1}{1 + \gamma_{\pm}} - \frac{e^{-2\gamma_{\pm} R - \gamma_{\pm} e^{-R} - \gamma_{\pm} R}}{1 - \gamma_{\pm}^2} \right]$ |
| HS | $\begin{cases} \left[\frac{\gamma_{+} - \frac{1}{2}(1+\lambda)(1+e^{-\gamma_{+} R})}{1+e^{-\gamma_{+} R}} \right] \left[\frac{\gamma_{-} - \frac{1}{2}(1+\lambda)(1-e^{-\gamma_{-} R})}{1-e^{-\gamma_{-} R}} \right] = \frac{1}{4}(1-\lambda)^2 \\ \left[\frac{\gamma_{+} - (1+e^{-\gamma_{+} R})}{1+e^{-\gamma_{+} R}} \right] = \frac{1-e^{-R}}{1+e^{-R}} \left[\frac{\gamma_{-} - (1-e^{-\gamma_{-} R})}{1-e^{-\gamma_{-} R}} \right] \end{cases}$ |
| RS | $\gamma_{\pm} = \frac{(1 \pm \lambda e^{-R})(1 \pm e^{-\gamma_{\pm} R})}{1 \pm e^{-R}}$ |

TABLE 4.5: Asymptotic R-Dependence of Second Order Energies.

| Procedure | $\pm E^{(2)}$ |
|--------------|--|
| Exact* | $-\frac{1}{2} e^{-2R} + O(e^{-3R})$ |
| Polarization | $-e^{-2R} + O(e^{-3R})$ |
| EL-HAV | $-\frac{1}{2} e^{-2R} + O(e^{-3R})$ |
| MS-MA | $\mp \frac{1}{2} e^{-3R} + O(e^{-4R})$ |
| HS | $-\frac{1}{2} e^{-2R} + O(e^{-3R})$ |
| RS | $\pm \frac{1}{2} e^{-2R} + O(e^{-3R})$ |

* See text.

APPENDIX A. Notation for Chapters Two and Three.

The compact matrix notation used in Chapters Two and Three is called by Löwdin (see, for example, ref. 62) the "fat notation".

i) Matrices are denoted by fat symbols; e.g. in Eq. (2.13),

$$\mathbb{E} = \begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \dots & \epsilon_{1s} \\ \epsilon_{21} & \epsilon_{22} & \dots & \epsilon_{2s} \\ \vdots & \vdots & \ddots & \vdots \\ \epsilon_{s1} & \epsilon_{s2} & \dots & \epsilon_{ss} \end{pmatrix} ;$$

$$\Phi = (\Phi_1, \Phi_2, \dots, \Phi_s).$$

ii) The sum and product of two matrices is defined in the usual way. The adjoint of a matrix and the multiplication of a matrix by a scalar is also defined in the ordinary way.

iii) The matrix of an operator \mathcal{O} in the space Φ is denoted by $\langle \Phi | \mathcal{O} | \Phi \rangle$, where $(\langle \Phi | \mathcal{O} | \Phi \rangle)_{kl} = \langle \Phi_k | \mathcal{O} | \Phi_l \rangle$.

iv) If \mathcal{F} is a set of nonorthogonal basis functions, the projector onto the linear manifold spanned by \mathcal{F} is

$$|\mathcal{F}\rangle \langle \mathcal{F} | \mathcal{F} \rangle^{-1} \langle \mathcal{F} |.$$

APPENDIX B. Algebraic Manipulations of Perturbation Equations.

B.1. Calculation of $\langle \Phi(N) | H - E | \Phi(N) \rangle$.

According to the perturbation equations (2.22)

$$(H^{(0)} + \lambda H^{(1)}) \Phi^{(0)} = \lambda H^{(1)} \Phi^{(0)} + \Phi^{(0)} \mathcal{E}^{(0)},$$

$$(H^{(0)} + \lambda H^{(1)}) \lambda \Phi^{(1)} + \lambda H^{(1)} \Phi^{(0)} = \lambda^2 H^{(1)} \Phi^{(1)} + \lambda \Phi^{(1)} \mathcal{E}^{(0)} + \lambda \Phi^{(0)} \mathcal{E}^{(1)},$$

$$\vdots$$

$$(H^{(0)} + \lambda H^{(1)}) \lambda^N \Phi^{(N)} + \lambda^N H^{(1)} \Phi^{(N-1)} = \lambda^{N+1} H^{(1)} \Phi^{(N)} + \sum_{\ell=0}^N \lambda^N \Phi^{(\ell)} \mathcal{E}^{(N-\ell)}$$

Adding these equations gives

$$H \Phi(N) = \lambda^{N+1} H^{(1)} \Phi^{(N)} + \sum_{k=0}^N \lambda^k \sum_{\ell=0}^k \Phi^{(\ell)} \mathcal{E}^{(k-\ell)}$$

Exchanging the order of summation over k and ℓ gives

$$H \Phi(N) = \lambda^{N+1} H^{(1)} \Phi^{(N)} + \sum_{\ell=0}^N \lambda^{\ell} \Phi^{(\ell)} \sum_{k=0}^{N-\ell} \lambda^k \mathcal{E}^{(k)}$$

$$\begin{aligned} &= \Phi(N) \mathcal{E}^{(N)} + \lambda^{N+1} H^{(1)} \Phi^{(N)} \\ &\quad - \sum_{\ell=1}^N \lambda^{\ell} \Phi^{(\ell)} \sum_{k=N-\ell+1}^N \lambda^k \mathcal{E}^{(k)} \end{aligned}$$

Collecting terms according to order in λ ,

$$H\Phi(N) = \Phi(N)\mathcal{E}(N) + \lambda^{N+1} \left\{ H^{(1)}\Phi^{(N)} - \sum_{k=0}^{N-1} \lambda^k \sum_{l=0}^{N-k-1} \Phi^{(k+l+1)} \mathcal{E}^{(N-l)} \right\}.$$

Hence,

$$\langle \Phi(N) | H - E | \Phi(N) \rangle =$$

$$= \langle \Phi(N) | \Phi(N) \rangle (\mathcal{E}(N) - E)$$

$$+ \lambda^{N+1} \left\{ \sum_{n=0}^N \lambda^n \langle \Phi^{(n)} | H^{(1)} | \Phi^{(N)} \rangle \right.$$

$$\left. - \sum_{n=0}^N \sum_{k=0}^{N-1} \lambda^{n+k} \sum_{l=0}^{N-k-1} \langle \Phi^{(n)} | \Phi^{(k+l+1)} \rangle \mathcal{E}^{(N-l)} \right\}.$$

Again collecting terms according to order in λ yields

$$\begin{aligned}
 \langle \Phi^{(N)} | H - E | \Phi^{(N)} \rangle &= \langle \Phi^{(N)} | \Phi^{(N)} \rangle (\mathcal{E}^{(N)} - E) \\
 &+ \lambda^{N+1} \sum_{n=0}^{N-1} \lambda^n \{ \langle \Phi^{(n)} | H^{(1)} | \Phi^{(N)} \rangle \\
 &\quad - \sum_{p=0}^n \sum_{q=0}^{N-n+p-1} \langle \Phi^{(p)} | \Phi^{(n+1-p+q)} \rangle \mathcal{E}^{(N-q)} \} \\
 &+ \lambda^{2N+1} \sum_{n=0}^{N-1} \lambda^n \{ \langle \Phi^{(n)} | H^{(1)} | \Phi^{(N)} \rangle \delta_{n0} \\
 &\quad - \sum_{p=0}^{N-n-1} \sum_{q=0}^p \langle \Phi^{(p+n+1)} | \Phi^{(N-p+q)} \rangle \mathcal{E}^{(N-q)} \}.
 \end{aligned}$$

B.2 Perturbation Energy Formulas.

In this Section, the Eq. (2.32) and (2.33), resulting from the full normalization condition Eq. (2.30) are proved. Also it is shown that $\mathcal{E}^{(n)}$ is a hermitean matrix.

First, however, it is convenient to establish some intermediate results. By taking the adjoint of Eq. (2.30) and adding it to the original equation, one obtains

$$\sum_{k=0}^n \langle \Phi^{(k)} | \Phi^{(n-k)} \rangle = 0; \quad n > 0. \quad (\text{B.1})$$

The following relation will be needed later:

$$\langle \phi^{(l-1)} | H^{(1)} | \phi^{(n-l)} \rangle = \langle \phi^{(l)} | H^{(1)} | \phi^{(n-l-1)} \rangle \quad (\text{B.2})$$

$$= \sum_{k=0}^{n-l} \langle \phi^{(l)} | \phi^{(n-l-k)} \rangle \epsilon^{(k)} + \sum_{k=0}^l \epsilon^{(k) \dagger} \langle \phi^{(l-k)} | \phi^{(n-l)} \rangle$$

This is proved by multiplying the ℓ -th order perturbation equation (2.22) from the left by $\phi^{(n-l) \dagger}$ and integrating,

$$\begin{aligned} & \langle \phi^{(n-l)} | H^{(0)} | \phi^{(l)} \rangle + \langle \phi^{(n-l)} | H^{(1)} | \phi^{(l-1)} \rangle \\ &= \sum_{k=0}^l \langle \phi^{(n-l)} | \phi^{(l-k)} \rangle \epsilon^{(k)}, \end{aligned} \quad (\text{B.3})$$

and multiplying the $(n-l)$ -th order equation from the left by $\phi^{(l)\dagger}$ and integrating,

$$\begin{aligned} \langle \phi^{(l)} | H^{(l)} | \phi^{(n-l)} \rangle + \langle \phi^{(l)} | H^{(1)} | \phi^{(n-l-1)} \rangle \\ = \sum_{k=0}^{n-l} \langle \phi^{(l)} | \phi^{(n-l-k)} \rangle \epsilon^{(k)} \end{aligned} \quad (\text{B.4})$$

Taking the adjoint of Eq. (B.3) and subtracting it from Eq. (B.4) yields Eq. (B.2).

From Eq. (2.29)

$$\epsilon^{(p)} = \langle \phi^{(p)} | H^{(1)} | \phi^{(p-1)} \rangle + \epsilon^{(0)} \langle \phi^{(p)} | \phi^{(p)} \rangle - \sum_{k=0}^{p-1} \langle \phi^{(p)} | \phi^{(p-k)} \rangle \epsilon^{(k)}$$

Application of Eq. (B.2) q times yields

$$\begin{aligned} \epsilon^{(p)} = \langle \phi^{(q)} | H^{(1)} | \phi^{(p-q-1)} \rangle + \sum_{l=0}^q \sum_{k=0}^l \epsilon^{(k)\dagger} \langle \phi^{(l-k)} | \phi^{(p-k)} \rangle \\ - \sum_{l=1}^q \sum_{k=0}^{p-l} \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \epsilon^{(k)} - \sum_{k=0}^{p-1} \langle \phi^{(p)} | \phi^{(p-k)} \rangle \epsilon^{(k)} \end{aligned}$$

Interchanging the order of summation gives

$$\begin{aligned} \mathcal{E}^{(p)} &= \langle \phi^{(q)} | H^{(1)} | \phi^{(p-q-1)} \rangle + \sum_{k=0}^q \mathcal{E}^{(k)} \dagger \sum_{l=0}^{q-k} \langle \phi^{(l)} | \phi^{(p-k-l)} \rangle \\ &= \sum_{k=0}^{p-q-1} \sum_{l=0}^q \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \mathcal{E}^{(k)} + \sum_{k=p-q}^{p-1} \sum_{l=0}^{p-k} \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \mathcal{E}^{(k)}. \end{aligned}$$

The final term vanishes by the normalization condition Eq. (B.1).

Hence,

$$\begin{aligned} \mathcal{E}^{(p)} &= \langle \phi^{(q)} | H^{(1)} | \phi^{(p-q-1)} \rangle + \sum_{k=0}^q \mathcal{E}^{(k)} \dagger \sum_{l=0}^{q-k} \langle \phi^{(l)} | \phi^{(p-k-l)} \rangle \\ &= \sum_{k=0}^{p-q-1} \sum_{l=0}^q \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \mathcal{E}^{(k)}. \end{aligned} \quad (\text{B.5})$$

The desired proofs are given by the following applications of

Eq. (B.5):

Put $p=n$, $q=n-1$:

$$\begin{aligned} \mathcal{E}^{(n)} &= \langle \phi^{(n-1)} | H^{(1)} | \phi^{(0)} \rangle - \sum_{l=0}^{n-1} \langle \phi^{(l)} | \phi^{(n-l)} \rangle \mathcal{E}^{(0)} \\ &\quad + \sum_{k=0}^{n-1} \mathcal{E}^{(k)} \dagger \sum_{l=0}^{n-k-1} \langle \phi^{(l)} | \phi^{(n-k-l)} \rangle. \end{aligned}$$

The coefficient of $\mathbb{E}^{(k)\dagger}$ is simplified by using Eq. (2.30):

$$\begin{aligned}\mathbb{E}^{(n)} &= \langle \phi^{(n-1)} | H^{(1)} | \phi^{(0)} \rangle + \langle \phi^{(0)} | \phi^{(n)} \rangle \mathbb{E}^{(0)} \\ &\quad - \sum_{k=0}^{n-1} \mathbb{E}^{(k)\dagger} \langle \phi^{(n-k)} | \phi^{(0)} \rangle,\end{aligned}$$

or

$$\mathbb{E}^{(n)} = \mathbb{E}^{(n)\dagger}. \quad (\text{B.6})$$

Put $p=2n$, $q=n-1$:

$$\begin{aligned}\mathbb{E}^{(2n)} &= \langle \phi^{(n-1)} | H^{(1)} | \phi^{(n)} \rangle \\ &\quad + \sum_{k=0}^{n-1} \mathbb{E}^{(k)} \sum_{\ell=0}^{n-k-1} \langle \phi^{(\ell)} | \phi^{(2n-k-\ell)} \rangle \\ &\quad - \sum_{k=0}^n \sum_{\ell=0}^{n-1} \langle \phi^{(\ell)} | \phi^{(2n-\ell-k)} \rangle \mathbb{E}^{(k)}.\end{aligned}$$

Or,

$$\mathcal{E}^{(2n)} = \langle \phi^{(n-1)} | H^{(1)} | \phi^{(n)} \rangle$$

$$= \sum_{k=1}^n \sum_{\ell=0}^{k-1} \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle \mathcal{E}^{(k)}$$

$$+ \sum_{k=1}^{n-1} \sum_{\ell=0}^{n-k-1} \left\{ \mathcal{E}^{(k)} \langle \phi^{(\ell)} | \phi^{(2n-k-\ell)} \rangle \right. \\ \left. - \langle \phi^{(\ell)} | \phi^{(2n-k-\ell)} \rangle \mathcal{E}^{(k)} \right\}$$

$$- \frac{1}{2} \left\{ \mathcal{E}^{(\omega)} \langle \phi^{(n)} | \phi^{(n)} \rangle - \langle \phi^{(n)} | \phi^{(n)} \rangle \mathcal{E}^{(\omega)} \right\}.$$

In the one-dimensional case, when all of the quantities in this equation are scalars, the Eq. (2.6) results. In general, the equation is simplified by using $\mathcal{E}^{(2n)} = \frac{1}{2} (\mathcal{E}^{(2n)} + \mathcal{E}^{(2n)\dagger})$:

$$\mathcal{E}^{(2n)} = \frac{1}{2} \left\{ \langle \phi^{(n-1)} | H^{(1)} | \phi^{(n)} \rangle + \langle \phi^{(n)} | H^{(1)} | \phi^{(n-1)} \rangle \right\}$$

$$- \frac{1}{2} \sum_{k=1}^n \sum_{l=0}^{k-1} \left\{ \langle \phi^{(n-k+l)} | \phi^{(n-l)} \rangle \mathcal{E}^{(k)} + \mathcal{E}^{(k)} \langle \phi^{(n-l)} | \phi^{(n-k+l)} \rangle \right\}$$

(B.7)

$$+ \frac{1}{2} \sum_{k=1}^{n-1} \sum_{l=0}^{n-k-1} \mathcal{E}^{(k)} \left\{ \langle \phi^{(l)} | \phi^{(2n-k-l)} \rangle - \langle \phi^{(2n-k-l)} | \phi^{(l)} \rangle \right\}$$

$$- \frac{1}{2} \sum_{k=1}^{n-1} \sum_{l=0}^{n-k-1} \left\{ \langle \phi^{(l)} | \phi^{(2n-k-l)} \rangle - \langle \phi^{(2n-k-l)} | \phi^{(l)} \rangle \right\} \mathcal{E}^{(k)}$$

From Eq. (2.30)

$$\sum_{l=0}^{n-k-1} \langle \phi^{(l)} | \phi^{(2n-k-l)} \rangle = \begin{cases} -\frac{1}{2} \langle \phi^{(\frac{2n-k}{2})} | \phi^{(\frac{2n-k}{2})} \rangle - \sum_{l=0}^{\frac{k-2}{2}} \langle \phi^{(n-k+l)} | \phi^{(n-l)} \rangle, & k \text{ even} \\ -\sum_{l=0}^{\frac{k-1}{2}} \langle \phi^{(n-k+l)} | \phi^{(n-l)} \rangle, & k \text{ odd} \end{cases} \quad (\text{B.8})$$

Substituting Eq. (B.8) into Eq. (B.7) yields Eq. (2.33).

Put $p=2n-1$, $q=n$:

By steps similar to those used to derive Eq. (2.33), one obtains Eq. (2.32).

APPENDIX C. Partitioning Technique Approach to Degenerate, Almost Degenerate, and Exchange Perturbation Theory.

It is the purpose of this Appendix to clarify the connection between the formalism of Chapter Two and the partitioning technique. Only the degenerate case will be treated in detail.

The basic notion of partitioning goes back to Van Vleck,³⁶ Lennard-Jones,⁶³ Brillouin,⁶⁴ and others in the early days of quantum mechanics. Lowdin and his coworkers⁶⁵ have developed the partitioning techniques into a very elegant and powerful approach to perturbation theory.

It is convenient to first quote some results of Lowdin.⁷⁰ Let Ψ and E be an eigenfunction and eigenvalue of the hamiltonian H ,

$$(H - E) \Psi = 0. \quad (C.1)$$

The Hilbert space of H is divided into two subspaces. The first is spanned by the set of functions $\phi_1^{(0)}, \phi_2^{(0)}, \dots, \phi_S^{(0)}$ and is characterized by the projection operator \mathcal{O} . The second subspace is spanned by an infinite set of functions and is characterized by the projector $P = 1 - \mathcal{O}$. These two operators satisfy

$$\mathcal{O}^2 = \mathcal{O} = \mathcal{O}^\dagger; \quad P^2 = P = P^\dagger; \quad \mathcal{O}P = P\mathcal{O} = 0.$$

In the partitioning technique, the Eq. (C.1) is replaced by

$$\mathcal{O}(\tilde{H} - E)\mathcal{O}\phi = 0, \quad (C.2)$$

where

$$\tilde{H} = H + H T(E) H,$$

and

$$T(E) = P[\alpha O + P(E-H)P]^{-1}P,$$

with $\alpha \neq 0$ but otherwise arbitrary. Eq. (C.2) is equivalent to the secular equation

$$\langle \Phi^{(0)} | \tilde{H} - E | \Phi^{(0)} \rangle = 0. \quad (C.3)$$

This is not an ordinary secular equation since \tilde{H} is a function of E . The usual approach is to solve Eq. (C.3) by an iterative process. For the degenerate case, writing

$$H = H^{(0)} + \lambda H^{(1)},$$

where

$$(H^{(0)} - \epsilon^{(0)}) \phi_k^{(0)} = 0, \quad 1 \leq k \leq S,$$

allows $T(E)$ to be written

$$T(E) = P[\alpha O + P(\epsilon^{(0)} - H^{(0)})P - P(\lambda H^{(1)} + \epsilon^{(0)} - E)P]^{-1}P.$$

Now defining

$$R_0 = P[\alpha O + P(\epsilon^{(0)} - H^{(0)})P]^{-1}P,$$

and using the "fundamental identity"

$$(A-B)^{-1} = A^{-1} + A^{-1} B (A-B)^{-1}$$

yields

$$T(E) = R_0 + R_0 (\lambda H^{(1)} + \epsilon^{(0)} - E) T(E), \quad (C.4)$$

This relation allows $T(E)$ to be approximated successively.

It is possible, as Löwdin⁶⁶ in the nondegenerate case and as Choi⁶⁷ and Goscinski and Löwdin⁶⁸ in the degenerate case have shown, to obtain the Rayleigh-Schrödinger expansion of the energy and the wavefunction by iterating Eq. (C.4) and expanding the roots of the secular equation (C.3) in powers of λ .

Of course, the expansion (C.4) can have a greater radius of convergence than the expansion in powers of λ of the roots E of the secular equation (C.3). Furthermore, given $T(E)$ the secular equation can be solved by techniques which avoid power series expansions.

Intermediate Normalization. In applications of the partitioning technique, the natural choice of normalization is "intermediate" normalization,

$$\langle \phi^{(0)} | \Phi \rangle = \langle \phi^{(0)} | \phi^{(0)} \rangle = 1, \quad (C.5)$$

rather than the full normalization chosen in Chapter Two. Thus it is necessary to derive the expressions for $\epsilon^{(n)}$ and $\phi^{(n)}$ which are applicable for the normalization Eq. (C.5).

To avoid confusion with the results using full normalization, subscripts rather than superscripts will be used to denote order in intermediate normalization. It is also convenient to absorb λ into the definitions of the perturbation terms and to define

$$V = \lambda H^{(1)},$$

$$V' = V - (E - E_0),$$

$$\epsilon'_k = \begin{cases} \epsilon_0 + \epsilon_1 - E & , k=1 \\ \epsilon_k & , k \neq 1 \end{cases}.$$

Expanding Eq. (C.5) in powers of λ yields

$$\langle \phi_0 | \phi_n \rangle = 0, \quad n \geq 1. \quad (C.6)$$

Multiplying Eq. (2.22) from the left by ϕ_0^\dagger and integrating gives

$$\epsilon_n = \langle \phi_0 | V | \phi_{n-1} \rangle. \quad (C.7)$$

Eq. (C.6) allows $N^{(n)}$ to be omitted from Eq. (2.34) so that the perturbation wavefunctions are

$$\phi_{n+1} = R_0 V' \phi_n - \sum_{k=1}^n R_0 \phi_{n+1-k} \epsilon'_k.$$

Iterating this equation, it follows that

$$\phi_{n+1} = (R_0 V')^{n+1} \phi_0 - \sum_{\ell=0}^{n-1} \sum_{k=1}^{n-\ell} (R_0 V')^\ell R_0 \phi_{n+1-\ell-k} \epsilon'_k \quad (C.8)$$

Expansion of $T(E)$. Iteration of Eq. (C.4) $(2N-1)$ times yields

$$T(E) = T_{2N-1}(E) + (R_0 V')^{2N} T(E), \quad (C.9)$$

where

$$T_{2N-1}(E) = R_0 \sum_{n=0}^{\infty} (V' R_0)^n. \quad (C.10)$$

With the neglect of the second term in Eq. (C.9) the secular equation (C.3) is

$$|\langle \phi_0 | H_0 + V + V T_{2N-1}(E) V - E | \phi_0 \rangle| = 0. \quad (C.11)$$

It can now be shown that the roots of Eq. (C.11) are identical,
through terms $O(\lambda^{2N+1})$, to the roots of the secular equation
(2.26).

This theorem is proved by using Eq. (C.8) and (C.10) and the fact that $R_0 \phi_0 = 0$, to obtain

$$T_{2N-1}(E) V \phi_0 = \sum_{n=0}^{2N-1} \phi_{n+1} + \sum_{n=1}^{2N-1} \sum_{\ell=0}^{n-1} \sum_{k=1}^{n-\ell} (R_0 V')^\ell R_0 \phi_{n+1-\ell-k} \epsilon'_k$$

Substitution of this result into Eq. (C.11) and the use of Eq. (C.7) gives

$$0 = \langle \phi_0 | H_0 + V + V T_{2N-1}(E) V - E | \phi_0 \rangle$$

$$\sum_{n=0}^{2N+1} \mathbb{E}_n - E$$

$$+ \sum_{n=1}^{2N-1} \sum_{l=0}^{n-1} \sum_{k=1}^{n-l} \langle \phi_{l+1} | \phi_{n+1-l-k} \rangle \mathbb{E}'_k$$

$$+ \sum_{n=2}^{2N-1} \sum_{l=0}^{n-1} \sum_{k=1}^{n-l} \sum_{i=0}^{l-1} \sum_{j=1}^{l-i} \mathbb{E}'_j \langle \phi_{l+1-i-j} | R_0 (V' R_0)^t | \phi_{n+1-l-k} \rangle \mathbb{E}'_k$$

rearranging the order of summation in the last two terms gives

$$\sum_{n=0}^{2N+1} \mathbb{E}_n - E$$

$$0 = + \sum_{n=1}^{N-1} \sum_{l=1}^n \langle \phi_l | \phi_{n+1-l} \rangle \sum_{k=1}^{2N-n} \mathbb{E}'_k$$

$$+ \sum_{n=1}^{2N-2} \mathbb{E}'_n \sum_{p=0}^{2N-n-2} \sum_{t=0}^p \sum_{u=0}^{p-t} \langle \phi_{p+1} | R_0 (V' R_0)^t | \phi_{p-t+1-u} \rangle \sum_{k=1}^{2N-n-p-1} \mathbb{E}'_k$$

It is now clear that, in the summations over k the upper limit may be replaced by $2N+1$ if terms $O(\lambda^{2N+2})$ are neglected.

Hence,

$$0 = \left| \begin{aligned} &1 + \sum_{n=1}^{2N+1} \sum_{\ell=1}^n \langle \phi_{\ell} | \phi_{n+1-\ell} \rangle \\ &+ \sum_{n=1}^{2N+2} \mathbb{E}_n' + \sum_{p=0}^{2N+2} \sum_{t=0}^p \sum_{v=0}^{p-t} \langle \phi_{v+1} | R_0(V'R_0)^t | \phi_{p-t+1-v} \rangle \end{aligned} \right|$$

$$\times \left| \sum_{n=0}^{2N+1} \mathbb{E}_n - E + O(\lambda^{2N+2}) \right|$$

Assuming that the first determinant is nonvanishing yields

$$0 = \left| \sum_{n=0}^{2N+1} \mathbb{E}_n - E + O(\lambda^{2N+2}) \right|_0. \quad (C.12)$$

Hence, the energies determined by Eq. (C.11) are identical with the energies determined by Eq. (C.12) through $O(\lambda^{2N+1})$. Furthermore, it was shown in Chapter Two that the change from intermediate to full normalization also affects the roots of Eq. (2.26) by

$O(\lambda^{2N+2})$ terms. Hence, it follows that the roots of secular equations (C.11) and (2.26) differ by $O(\lambda^{2N+2})$ terms.

ON THE MODIFICATION OF EXCHANGE PERTURBATION THEORIES *

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A transformation of the unperturbed Hamiltonian in the Eisenschitz-London, Van der Avoird, or Hirschfelder HAV exchange perturbation theories is suggested, which modifies the second order energy to produce the correct long-range behavior.

1. INTRODUCTION

In recent applications [1,2,9] of the Eisenschitz-London [3], Van der Avoird [4], or Hirschfelder HAV [5] perturbation theories for the exchange forces between atoms, it has become apparent that the second order energy in these schemes fails at large interatomic separations R to equal the second order dispersion energy (no exchange), even though "exchange effects" are negligible at these separations. In the previous calculations [1,2], the correct long-range limit was obtained by a variation-perturbation approach. In this note we suggest an alternative method for obtaining the correct limit, by introducing a transformation of the unperturbed Hamiltonian of a type originally suggested by Feenberg [6].

2. PERTURBATION THEORIES

In this section we review briefly the usual Rayleigh-Schrödinger (unsymmetrized) theory and the Eisenschitz-London, Van der Avoird or Hirschfelder HAV theory for the long-range interactions between atoms. The problem may be stated succinctly by making use of the wave operator formalism [4,7]. Conventionally long-range interactions are computed from

$$E = E_0 + \langle \phi_0 | V + VT | \phi_0 \rangle, \quad (1)$$

where

$$T = R_0 + R_0 V' T, \quad V' = V - (E - E_0), \\ R_0 = P(E_0 - H_0)^{-1} P, \quad H_0 \phi_0 = E_0 \phi_0, \quad (2)$$

$$P = 1 - |\phi_0\rangle\langle\phi_0|,$$

where H_0 is a sum of isolated atom Hamiltonians. ϕ_0 is product of isolated atom wavefunctions, and V contains the interatomic interactions. Substitution of eqs. (2) into (1) and iteration yields

$$E = E_0 + \epsilon_1 + \epsilon_2 + \epsilon_3 + \dots$$

where

$$\epsilon_1 = \langle \phi_0 | V | \phi_0 \rangle,$$

$$\epsilon_2 = \langle \phi_0 | VR_0 V | \phi_0 \rangle,$$

$$\epsilon_3 = \langle \phi_0 | VR_0 (V - \epsilon_1 R_0 V) | \phi_0 \rangle.$$

When exchange effects are not negligible, the above treatment is not sufficient because ϕ_0 does not have the symmetry of $H = H_0 + V$. Let A be the projection operator onto the subspace of desired symmetry. Then the interaction energy may be computed from

$$E = E_0 + \frac{\langle \phi_0 | VA + VT V | \phi_0 \rangle}{\langle \phi_0 | A | \phi_0 \rangle}, \quad (3)$$

where

$$T = PR_0 P + PR_0 UT \quad (4)$$

and the former definition of P is replaced by

$$P = A - \frac{A |\phi_0\rangle\langle\phi_0| A}{\langle \phi_0 | A | \phi_0 \rangle},$$

and

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Table 1.

Energy of H_2 (in cm^{-1}). Here $c = \langle \phi_0 | A | \phi_0 \rangle^{-1}$ and λ is the value of the parameter in eq. (5) which optimizes the expectation value of the Hamiltonian in refs. [1] and [9].

| | R | λ | c | $E_0 + E_1 + E_2 - E$ (exact) | $E_0 + E_1 + \lambda E_2 - E$ (exact) | $E_0 + E_1 + c E_2 - E$ (exact) | E (exact) |
|---------------|-----|-----------|------|-------------------------------|---------------------------------------|---------------------------------|-------------|
| Ground State | 4 | 1.36 | 1.93 | 427.0 | 177.8 | -214.2 | 3592.6 |
| $1 \sum^+$ | 6 | 1.39 | 2.00 | 25.5 | 9.4 | -16.1 | 178.9 |
| g | 8 | 1.92 | 2.00 | 3.8 | 0.1 | -0.2 | 11.7 |
| Excited State | 4 | 1.42 | 2.07 | 169.6 | 39.6 | -158.0 | -1453.3 |
| $3 \sum^+$ | 6 | 1.89 | 2.00 | 23.5 | 4.4 | 2.2 | -41.2 |
| u | 8 | 1.98 | 2.00 | 3.8 | 0.3 | 0.3 | 4.3 |

Table 2.

Energy of the One-Dimensional Model. Here $c = \langle \phi | A | \phi \rangle^{-1} = 2/(1 \pm \exp(-R^2))$ and λ is the value of the parameter in eq. (5) which optimizes the expectation value of the Hamiltonian in ref. [2].

| | R | λ | c | $E_0 + E_1 + E_2 - E$ (exact) | $E_0 + E_1 + \lambda E_2 - E$ (exact) | $E_0 + E_1 + c E_2 - E$ (exact) | E (exact) |
|------------------------|-----|-----------|--------|-------------------------------|---------------------------------------|---------------------------------|-------------|
| Gerade Ground State | 0.8 | 0.3302 | 1.3095 | -0.1551 | 0.0180 | -0.2351 | 0.3308 |
| | 1.0 | 0.4528 | 1.4621 | -0.0857 | 0.0149 | -0.1706 | 0.2940 |
| | 1.2 | 0.5964 | 1.6169 | -0.0469 | 0.0161 | -0.1432 | 0.2806 |
| | 2.0 | 1.3935 | 1.9640 | 0.0653 | 0.0355 | -0.0062 | 0.3502 |
| | 2.6 | 1.6236 | 1.9977 | 0.0473 | 0.0272 | 0.0151 | 0.4307 |
| | 3.0 | 1.6077 | 1.9998 | 0.0279 | 0.0147 | 0.0063 | 0.4604 |
| | 5.0 | 1.8314 | 2.0000 | 0.0072 | 0.0014 | 0.0002 | 0.4895 |
| Ungerade Excited State | 0.8 | 0.3457 | 4.2310 | -0.2404 | 0.9426 | -1.6381 | 1.1403 |
| | 1.0 | 0.4523 | 3.1641 | -0.0819 | 0.0171 | -0.3749 | 0.9314 |
| | 1.2 | 0.5536 | 2.6209 | -0.0343 | 0.0088 | -0.1908 | 0.7870 |
| | 2.0 | 0.9494 | 2.0373 | 0.0025 | 0.0037 | -0.0316 | 0.5232 |
| | 2.6 | 1.3268 | 2.0024 | 0.0139 | 0.0056 | -0.0119 | 0.4776 |
| | 3.0 | 1.5031 | 2.0002 | 0.0164 | 0.0062 | -0.0040 | 0.4740 |
| | 5.0 | 1.8315 | 2.0000 | 0.0072 | 0.0014 | 0.0002 | 0.4895 |

$$U = \left(1 - \frac{A|\phi_0\rangle\langle\phi_0|}{\langle\phi_0|A|\phi_0\rangle}\right) V'.$$

Substitution of eq. (4) into (3) and iteration yields

$$E = E_0 + E_1 + E_2 + E_3 + \dots,$$

where

$$E_1 = \langle\phi_0|VA|\phi_0\rangle/\langle\phi_0|A|\phi_0\rangle,$$

$$E_2 = \langle\phi_0|VPR_0PV|\phi_0\rangle/\langle\phi_0|A|\phi_0\rangle,$$

$$E_3 = \langle\phi_0|VPR_0P(V-E_1)PR_0PV|\phi_0\rangle/\langle\phi_0|A|\phi_0\rangle.$$

The difficulty is that, for the systems considered,

$$\lim_{R \rightarrow \infty} \frac{E_2}{\epsilon_2} \neq 1,$$

so that $E = E_0 + E_1 + E_2$ is a bad approximation for R large.

3. PERTURBATION-VARIATION APPROACH

A better approximation was obtained [1,2] by computing the expectation value of H with the variational wave function

$$\tilde{\psi} = A\phi_0 + \lambda PR_0P\phi_0, \quad (5)$$

where the variational parameter λ was energy optimized, with the result

$$\tilde{E} = \langle\tilde{\psi}|H|\tilde{\psi}\rangle/\langle\tilde{\psi}|\tilde{\psi}\rangle = E_0 + E_1 + \lambda E_2,$$

and

$$\lim_{R \rightarrow \infty} \lambda E_2/\epsilon_2 = 1.$$

This result has been emphasized recently by Goscinski and Brändas [8].

4. THE FEENBERG TRANSFORMATION [6]

The computation of λ requires a knowledge of E_2 and E_3 [8]. A procedure for removing the long-range defect with a knowledge of E_2 only is as follows. Instead of iterating eq. (4), one iterates

$$T = cPR_0P + cPR_0UT + (1-c)T, \quad (6)$$

which is strictly equivalent to eq. (4) if c is an arbitrary constant, and obtains through second order

$$E = E_0 + E_1 + cE_2.$$

This method is equivalent to replacing [6] $(H_0 - E_0)$

by $(1/c)(H_0 - E_0)$ and V by $V - (1-c/c)(H_0 - E_0)$ in eq. (4).

In order to obtain the correct long range behavior, the constant c must satisfy

$$\lim_{R \rightarrow \infty} cE_2/\epsilon_2 = 1. \quad (7)$$

For the systems previously considered, the choice

$$c = \langle\phi_0|A|\phi_0\rangle^{-1} \quad (8)$$

satisfies eq. (7). In tables 1 and 2 we present a comparison between the variational approach and Feenberg transformation.

For the systems considered, the choice of eq. (8) is consistent if the energy is computed through third order. Iteration of eq. (6) twice yields

$$E = E_0 + c(2-c)E_2 + c^2E_3.$$

In these examples, $c \rightarrow 2$ and $E_3 \rightarrow \frac{1}{2}E_2$ as $R \rightarrow \infty$, so $E \rightarrow E_0 + 2E_2$ which is equal to $E_0 + \epsilon_1 + \epsilon_2$ for large R .

In general, however, the computation of E_3 requires a large increase in the number and complexity of integrals over those needed to compute E_2 . For this reason the Feenberg transformation offers a practical advantage over the variational approach. The significance of the choice of c which we have made escapes us, however.

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APPENDIX E. Direct Calculation of Second Order Energies for the
Delta-Function Model.

As was shown in Section 4.1, the second order energies may be evaluated by a quadrature involving the function ${}^{\pm}\chi$ defined by

$$(H^{(0)} - \epsilon^{(0)}) {}^{\pm}\chi + A_{\pm} (H^{(1)} - {}^{\pm}E^{(1)}) \phi^{(0)} = 0, \quad (\text{E.1})$$

$$\langle {}^{\pm}\chi | \phi^{(0)} \rangle = 0. \quad (\text{E.2})$$

The second order energies are given by

$${}^{\pm}E^{(2)}(\text{EL-HAV}) = \frac{\langle {}^{\pm}\chi | A_{\pm} (H^{(1)} - {}^{\pm}E^{(1)}) | \phi^{(0)} \rangle}{\langle \phi^{(0)} | A_{\pm} | \phi^{(0)} \rangle}, \quad (\text{E.3})$$

$${}^{\pm}E^{(2)}(\text{MS-MA}) = \frac{\langle {}^{\pm}\chi | H^{(1)} | \phi^{(0)} \rangle}{\langle \phi^{(0)} | A_{\pm} | \phi^{(0)} \rangle}, \quad (\text{E.4})$$

$${}^{\pm}E^{(2)}(\text{HS}) = \frac{\langle {}^{\pm}\chi | H^{(1)} | \phi^{(0)} \rangle - \frac{1}{2}({}^{\pm}E^{(1)} - E^{(1)}) \langle {}^{\pm}\chi | I | \phi^{(0)} \rangle}{\langle \phi^{(0)} | A_{\pm} | \phi^{(0)} \rangle}, \quad (\text{E.5})$$

Introducing the definitions of $H^{(0)}$, $H^{(1)}$, $\epsilon^{(0)}$, ${}^{\pm}E^{(1)}$, $\phi^{(0)}$, and A_{\pm} , Eq. (E.1) may be written

$$\left[\frac{d^2}{dx^2} + 2\delta(x+a) - 1 \right] {}^{\pm}\chi + [\delta(x-a) + {}^{\pm}E^{(1)}] e^{-|x+a|} \\ {}^{\pm}[\delta(x+a) + {}^{\pm}E^{(1)}] e^{-|x-a|} = 0,$$

where $a = R/2$,

or, omitting the (\pm) sub- and superscripts,

$$\left[\frac{d^2}{dx^2} - 1\right]\chi + E^{(1)}e^{-|x+a|} \pm E^{(1)}e^{-|x-a|} = 0, \quad |x| \neq a; \quad (\text{E.6})$$

with the matching conditions

$$\frac{d}{dx}\chi \Big|_{x=a+} - \frac{d}{dx}\chi \Big|_{x=a-} + 2\chi(a) \pm e^{-R} = 0; \quad (\text{E.7})$$

$$\frac{d}{dx}\chi \Big|_{x=a+} - \frac{d}{dx}\chi \Big|_{x=a-} + e^{-R} = 0; \quad (\text{E.8})$$

$$\chi(a+) - \chi(a-) = 0; \quad (\text{E.9})$$

$$\chi(a+) - \chi(a-) = 0. \quad (\text{E.10})$$

The general solution of Eq. (E.6)

$$\chi = \begin{cases} A^{(1)}e^{-x} - A^{(1)}\delta^{(1)}xe^{-x} & ; x > a \\ \left[B^{(1)}e^x + C^{(1)}e^{-x} + B^{(1)}\delta^{(1)}xe^x - C^{(1)}\delta^{(1)}xe^{-x} \right] & ; |x| < a \\ D^{(1)}e^x + D^{(1)}\gamma^{(1)}xe^x & ; x < -a, \end{cases} \quad (\text{E.11})$$

where

$$A^{(0)} = \frac{1}{2} (e^{-a} \pm e^a),$$

$$B^{(0)} = \pm \frac{1}{2} e^{-a},$$

$$C^{(0)} = \frac{1}{2} e^{-a},$$

$$D^{(0)} = \frac{1}{2} (e^a \pm e^{-a}),$$

$$\gamma^{(1)} = -E^{(1)} = \frac{\pm e^{-R} + e^{-2R}}{1 + (1+R)e^{-R}},$$

and $A^{(1)}$, $B^{(1)}$, $C^{(1)}$, $D^{(1)}$ are chosen to satisfy Eq. (E.7)

through (E.10). Thus,

$$\begin{pmatrix} 0 & e^{-a} & -e^a & e^{-a} \\ -e^{-a} & -e^a & e^{-a} & 0 \\ 0 & e^{-a} & e^a & -e^{-a} \\ e^{-a} & -e^{-a} & -e^{-a} & 0 \end{pmatrix} \begin{pmatrix} A^{(1)} \\ B^{(1)} \\ C^{(1)} \\ D^{(1)} \end{pmatrix} = \begin{pmatrix} \gamma^{(1)} [1 + a \pm a e^{-R}] \mp e^{-R} \\ \pm \gamma^{(1)} - e^{-R} \\ -a \gamma^{(1)} \\ \pm a \gamma^{(1)} \end{pmatrix} \quad (\text{E.12})$$

These equations are not linearly independent, however, as may be verified by comparing the sum of the first and third equations with the sum of the second and fourth equations, and making use of the definition of $\gamma^{(1)}$. Thus, one of the Eqs. (E.12) must be replaced by another which is linearly independent. This is just the freedom required to enable the normalization condition, Eq. (E.2), to be satisfied. Making use of Eq. (E.11), Eq. (E.2) becomes

$$e^{-R-a} A^{(1)} + 2R e^{-a} B^{(1)} + e^{-a} (e^R - e^{-R}) C^{(1)} + e^{a-R} D^{(1)} = \frac{1}{2} [1 \pm (1+R) e^{-R}] \gamma^{(1)}. \quad (\text{E.13})$$

Eq. (E.13) now replaces the first equation in Eqs. (E.12). Then, $A^{(1)}$, $B^{(1)}$, $C^{(1)}$, $D^{(1)}$ can be obtained in a straightforward manner. The result is

$$\begin{aligned} A^{(1)} &= \frac{1}{2} \gamma^{(1)} e^a \left[\mp (2-R) + (1-R) e^{-R} \pm (3+3R+R^2) e^{-2R} \right] \\ &\quad + \frac{1}{2} e^{-R+a} [1 - (1+R) e^{-2R}], \\ B^{(1)} &= \frac{1}{4} \gamma^{(1)} e^{-a} [\mp (2+R)] + \frac{1}{2} e^{-R-a}, \\ C^{(1)} &= \frac{1}{4} \gamma^{(1)} e^{-a} [1-R \pm (3+3R+R^2) e^{-R}] - \frac{1}{2} (1+R) e^{-2R-a}, \\ D^{(1)} &= \frac{1}{4} \gamma^{(1)} e^a [1+R \pm (1+R)^2 e^{-R}] - \frac{1}{2} R e^{-R-a}. \end{aligned}$$

This completes the determination of $\pm \chi$.

In order to evaluate the second order energies, the following integrals are needed:

$$\begin{aligned} \langle \pm \chi | H^{(1)} | \phi_0 \rangle &= \gamma^{(1)} \left[-\frac{3}{4} e^{-2R} \mp \frac{1}{4} (3+3R+3R^2) e^{-3R} \right] \\ &\quad \pm \frac{1}{2} e^{-3R} [1 \pm (1+R) e^{-R}], \end{aligned}$$

$$\langle \pm \chi | I H^{(1)} | \phi^{(0)} \rangle = -\frac{1}{4} \gamma^{(1)} e^{-R} [1 \pm (1+R+R^2)e^{-R}] + \frac{1}{2} R e^{-3R},$$

$$\begin{aligned} \langle \pm \chi | I | \phi^{(0)} \rangle = & \frac{1}{4} \gamma^{(1)} [\mp 3 - R^2 e^{-R} \pm (1+R)(3+3R+R^2)e^{-2R}] \\ & + \frac{1}{2} e^{-R} [1 - (1+R)^2 e^{-2R}], \end{aligned}$$

With these integrals and Eq. (E.3) through (E.5), the asymptotic dependencies given in Table 4.5 are obtained.

APPENDIX F. Other Publications of Phillip R. Certain

Reprinted in this Appendix are the following articles, which report work completed at the Theoretical Chemistry Institute, Madison, Wisconsin.

1. "A Single Variable Variational Approximation for a Perturbed Schrödinger Equation", W. Byers Brown and Phillip R. Certain, Proc. Nat. Acad. Sci. 57, 1206 (1967).
2. "Comment on Van der Avoird's Wave Operator Formalism", R. E. Johnson and P. R. Certain, Chem. Phys. Letters, 1, 413 (1967).
3. "Calculation of Matrix Elements for One-Dimensional Quantum-Mechanical Problems", A. S. Dickinson and P. R. Certain, J. Chem. Phys., 49, 4209 (1968).
4. "Localized Orbitals for Arbitrary Molecular Wave Functions", P. R. Certain and J. O. Hirschfelder, Chem. Phys. Letters, 2, 274 (1968).

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A SINGLE VARIABLE VARIATIONAL APPROXIMATION FOR A PERTURBED SCHRÖDINGER EQUATION*

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Communicated by Joseph O. Hirschfelder, March 24, 1967

The difficulty in applying the Rayleigh-Ritz variational method to molecular systems lies in choosing the trial wave function, $\tilde{\psi}$. In this paper we consider a variational approximation for the ground state of the perturbed Schrödinger equation

$$(H_0 + V - E)\psi = 0, \quad (1)$$

where the perturbation V is a function of the configuration variables, and the ground state eigenfunction ψ_0 of H_0 is known. We write the trial wave function

$$\tilde{\psi} = F\psi_0, \quad (2)$$

but instead of guessing a specific form for F , we seek the best F which is a function of V only, $F = F(V)$. This leads to a Schrödinger-type equation

$$(h_0 + V - \tilde{E})F = 0 \quad (3)$$

in the single variable V , involving the approximate ground state eigenvalue $\tilde{E} (\geq E)$. Equation (3) is an ordinary linear differential equation which can be readily solved numerically.

The analogous first-order variation-perturbation theory has been derived recently by Kirtman and Benston,¹ and called by them the extended average energy method. They present their derivation as an extension of the Unsöld or average energy approximation,^{2, 3} which is equivalent to employing a first-order trial wave function of the form $\tilde{\psi}_1 = f\psi_0$ with $f = -(V - E_1)/\Delta E$, where ΔE is an average excitation energy. The functional minimization method used in this paper leads to essentially the same results as those of Kirtman and Benston.¹

Perturbed Schrödinger Equation.—Consider a system described by the n orthogonal curvilinear coordinates $\mathbf{q} = q_1, q_2, \dots, q_n$. Let the unperturbed Hamiltonian be (atomic units)

$$H_0 \equiv -1/2\nabla^2 + U_0,$$

where $U_0(\mathbf{q})$ is a function of the coordinates, and

$$\nabla^2 = \sum_{i=1}^n \frac{1}{h_i} \frac{\partial}{\partial q_i} \left(\frac{h}{h_i^2} \frac{\partial}{\partial q_i} \right),$$

where the $h_i(\mathbf{q})$ are the metric scale factors, and $h = h_1 h_2 \dots h_n$. Let $\psi_0(\mathbf{q})$ and E_0 be the lowest unperturbed eigenfunction (assumed real) and eigenvalue satisfying

$$(H_0 - E_0)\psi_0 = 0. \quad (4)$$

We are interested in the solution (ψ, E) of the perturbed Schrödinger equation (1) in the case in which the perturbation V is a function (not a differential operator) of the coordinates \mathbf{q} ; or more conveniently, in which

$$V = V(u) \quad \text{where } u = u(q) \text{ with range } (a, b). \quad (5)$$

The variable u may or may not be one of the coordinates q .

Variationally Reduced Schrödinger Equation.—We seek the best trial wave function of the form

$$\bar{\psi} = F(u)\psi_0(q) \quad (6)$$

by means of the Rayleigh-Ritz variation principle $\delta\bar{E} = 0$ with respect to arbitrary variations $\delta F(u)$, where the functional $\bar{E}[F]$ is defined by

$$\langle \bar{\psi}, (H_0 + V - \bar{E})\bar{\psi} \rangle = 0. \quad (7)$$

By substituting for $\bar{\psi}$ from (6), using the unperturbed Schrödinger equation (4) and rearranging, equation (7) may be rewritten

$$\langle \psi_0, \{ \frac{1}{2}(\nabla F)^2 + (V + E_0 - \bar{E})F^2 \} \psi_0 \rangle = 0. \quad (8)$$

Since $F = F(u)$, $(\nabla F)^2 = \left(\frac{dF}{du}\right)^2 (\nabla u)^2$, where $(\nabla u)^2 = \sum_{i=1}^n \frac{1}{h_i^2} \left(\frac{\partial u}{\partial q_i}\right)^2$. We define two functions of u , which involve only the unperturbed distribution:

$$P_0(u') = \langle \psi_0, \delta(u' - u)\psi_0 \rangle, \quad (9)$$

$$Q_0(u') = \langle \psi_0, \delta(u' - u)(\nabla u)^2 \psi_0 \rangle, \quad (10)$$

where $\delta(x)$ is the Dirac delta function. $P_0(u)$ is the probability density for the variable u in the unperturbed ground state, and is normalized to unity provided ψ_0 has unit norm,

$$\int_a^b P_0(u) du = \langle \psi_0, \psi_0 \rangle = 1.$$

In many cases $(\nabla u)^2$ will be a constant, say c ; then $Q_0 = cP_0$; but in general Q_0 differs from P_0 .

Equation (8) can now be written as the single integral

$$\int_a^b du \left\{ \frac{1}{2} Q_0 \left(\frac{dF}{du} \right)^2 + (V + E_0 - \bar{E}) F^2 P_0 \right\} = 0.$$

By carrying out a functional variation $\delta F(u)$ and setting $\delta\bar{E} = 0$ we obtain

$$\int_a^b du \left\{ -\frac{1}{2} \frac{d}{du} \left(Q_0 \frac{dF}{du} \right) + (V + E_0 - \bar{E}) F P_0 \right\} \delta F + \frac{1}{2} \left[Q_0 \frac{dF}{du} \delta F \right]_a^b = 0.$$

Since the variations δF are arbitrary, we must have

$$-\frac{1}{2} \frac{d}{du} \left(Q_0 \frac{dF}{du} \right) + (V + E_0 - \bar{E}) F P_0 = 0, \quad (11)$$

and

$$Q_0(a)F'(a) = Q_0(b)F'(b) = 0. \quad (12)$$

Equation (11) can be written in the form of the variationally reduced Schrödinger equation (3) where the single-variable unperturbed Hamiltonian is defined by

$$h_u = -\frac{1}{2} P_0^{-1} \frac{d}{du} \left(Q_0 \frac{d}{du} \right) + V_u.$$

The factor function F of interest is the ground state solution of (11) satisfying (12) which belongs to $L_2(a,b)$ with weight factor $P_0(u)$; that is, $\int_a^b P_0 F^2 du$ is finite. Note that $P_0 \geq 0$, and for the unperturbed ground state $P_0 > 0$ except possibly at the limits a, b . Equation (11) is an ordinary linear differential equation which can be readily solved by numerical methods. In a later section we discuss the explicit perturbation solution.

By integrating equation (11) over the range (a,b) and using (12), we see that the eigenvalue is given by

$$\tilde{E} = E_0 + \int_a^b P_0 V F du / \int_a^b P_0 F du.$$

This is a variationally reduced form of the so-called integral Hellmann-Feynman theorem.⁴

Generalizations.—There are two obvious generalizations.

(a) *Perturbation V :* The best approximation $\tilde{\psi} = F(u)\psi_0$ may still be found even though the perturbation $V = V(q)$ depends on variables other than u , and also if it contains differential operators in the Schrödinger representation. In the more general case equation (11) becomes

$$-\frac{1}{2} \frac{d}{du} \left(Q_0 \frac{dF}{du} \right) + WF + (E_0 - \tilde{E})P_0 F = 0,$$

where

$$W(u') = \langle \psi_0, V \delta(u - u') \psi_0 \rangle,$$

and may involve a differential operator with respect to u' .

(b) *Factor function F :* The procedure can clearly be generalized to allow F to depend on more than one variable, $F = F(\mathbf{u})$, $\mathbf{u} \equiv u_1, u_2, \dots, u_n$. However, this leads in general to a nonseparable partial differential equation of the form

$$-\frac{1}{2} \sum_{\alpha} \sum_{\beta} \frac{\partial}{\partial u_{\alpha}} \left(Q_{\alpha\beta} \frac{\partial F}{\partial u_{\beta}} \right) + (V + E_0 - \tilde{E})P_0 F = 0,$$

where, in an obvious notation,

$$Q_{\alpha\beta}(\mathbf{u}) = \langle \psi_0, \delta^m(\mathbf{u}' - \mathbf{u}) (\nabla u_{\alpha} \cdot \nabla u_{\beta}) \psi_0 \rangle.$$

Perturbation Approach.—We now turn to the first-order perturbation solution of equation (11). It is instructive to derive the relevant equations from the Hylleraas variational principle for the second-order energy, E_2 , as a function of a trial first-order wave function $\tilde{\psi}_1$:

$$\tilde{E}_2 = \langle \tilde{\psi}_1, (H_0 - E_0) \tilde{\psi}_1 \rangle + 2 \langle \tilde{\psi}_1, (V - E_1) \psi_0 \rangle \geq E_2, \quad (13)$$

where $E_1 = \langle \psi_0, V \psi_0 \rangle$ is the first-order energy. We expand F defined by equation (2) as a perturbation series $F = 1 + f + \dots$, where we have put $F_0 = 1$, $E_1 = f$, so that

$$\tilde{\psi}_1 = f \psi_0. \quad (14)$$

Then by substituting (14) into (13) and rearranging, we obtain

$$\tilde{E}_2 = \frac{1}{2} \langle \psi_0 | (\nabla f)^2 | \psi_0 \rangle + 2 \langle \psi_0 | (V - E_1) f | \psi_0 \rangle. \quad (15)$$

We again consider a perturbation $V(u)$ as described by (5), and seek the best first-order trial wave function of the form

$$\tilde{\psi}_1 = f(u) \psi_0(\mathbf{q}). \quad (16)$$

Then (15) can be reduced to

$$\tilde{E}_2 = \int_a^b du \left\{ \frac{1}{2} Q_0 \left(\frac{df}{du} \right)^2 + 2(V - E_1) P_0 f \right\},$$

where $P_0(u)$ and $Q_0(u)$ are defined as before by equations (9) and (10). By making the functional $\tilde{E}_2[f]$ stationary with respect to arbitrary variations $\delta f(u)$, we derive the equations

$$\frac{d}{du} \left(Q_0 \frac{df}{du} \right) = 2(V - E_1) P_0 \quad (17)$$

and $Q_0(a)f'(a) = Q_0(b)f'(b) = 0$.

Equation (17) has the same form as the first-order perturbation equation for a separable variable u (or a simple one-dimensional case), and can be integrated directly^{5, 8} to yield

$$f(u') = f(a) + \int_a^{u'} \frac{M(u)}{Q_0(u)} du \quad (18)$$

and hence,

$$\tilde{E}_2 = -\frac{1}{2} \int_a^b \frac{M^2(u)}{Q_0(u)} du, \quad (19)$$

where

$$\begin{aligned} M(u') &= 2 \langle \psi_0 | (V - E_1) \Delta(u' - u) | \psi_0 \rangle, \\ &= 2 \int_a^{u'} (V - E_1) P_0 du, \end{aligned} \quad (20)$$

where $\Delta(x)$ is the Heaviside unit-step function.

Equation (18) is essentially the same as that derived by Kirtman and Benston¹ by their extended average-energy method; our equation is simpler and slightly more general in that the variable u need not be a member of the \mathbf{q} 's. This result establishes that the extended average-energy method does indeed give the best first-order trial wave function of the form (16); that is, the one giving the lowest value of \tilde{E}_2 ($\geq E_2$ exact) as claimed by Kirtman and Benston.¹

Application to the Two-Electron Atom.—In this section we apply the foregoing theory to the ground state of the two-electron atom with atomic number Z . We take as our single variable $u = r_{12}$, the interelectron distance. The simplest application is to take the perturbation V to be the electron repulsion term $1/r_{12}$. In this case, we have (unit of length = Z Bohr) $\psi_0 = \pi^{-1} \exp(-r_1 - r_2)$, $E_0 = -Z^2$, $E_1 = \frac{5}{8}Z$. It follows from (9) that

$$P_0 = \frac{1}{2} u^2 \left(1 + 2u + \frac{4}{3} u^2 \right) e^{-2u},$$

and since $(\nabla r_{12})^2 = 2$, $Q_0 = 2P_0$. Unfortunately, it does not appear easy to solve (11) analytically (though a numerical solution could be easily obtained). We therefore turn to first-order perturbation theory. The integral (18) reduces to

$$f = \frac{1}{16Z} \left[5u + \ln \left(u^2 + \frac{3}{2} u + \frac{3}{4} \right) + \sqrt{3} \arctan \left(\frac{4u + 3}{\sqrt{3}} \right) \right] + \text{const.},$$

and the integral (19) is equal to¹⁶ $\bar{E}_2 = -0.135337$ Hartree. The accurate value is^{6,7} $E_2 = -0.157666$ Hartree. These results agree essentially with those of Kirtman and Benston.^{1,8}

A better starting point is to take the Hartree-Fock wave function $\psi_{HF} = \phi(r_1)\phi(r_2)$ as the unperturbed condition. We therefore seek the best correlation factor F in the trial wave function

$$\bar{\psi} = F(r_{12})\psi_{HF}(r_1, r_2). \quad (21)$$

We are even less able to solve the complete equation (11) analytically, but the first-order perturbation theory is still tractable, and not much harder. The first-order wave function can be written in the form $\bar{\psi}_1 = \psi_1^{HF} + \bar{\psi}_1^{\text{corr}}$ where $\psi_1^{HF} = \{f_{HF}(r_1) + f_{HF}(r_2)\}\psi_0$, and $\bar{\psi}_1^{\text{corr}} = F_1(r_{12})\psi_0$. The first-order Hartree factor is known analytically,⁹

$$f_{HF}(r) = -\frac{1}{8Z} \left[3 \int_0^{2r} (1 - e^{-t}) t^{-1} dt + 3(e^{-2r} - 1)/2r + 2e^{-2r} - 5r + 23/4 - 3 \ln 2 \right].$$

The Hylleraas second-order energy, defined by equation (13), can be written in the form¹⁰ $\bar{E}_2 = E_2^{HF} + \bar{E}_2^{\text{corr}}$, where⁹ $E_2^{HF} = -\frac{13}{804} + \frac{9}{64} \ln \left(\frac{3}{4} \right) = -0.111003$ Hartree, and

$$\bar{E}_2^{\text{corr}} = \frac{1}{2} \langle \psi_0, (\nabla f_{\text{corr}})^2 \psi_0 \rangle + 2 \langle \psi_0, \nabla f_{\text{corr}} \psi_0 \rangle, \quad (22)$$

where $f_{\text{corr}} = F_1(u)$ and the correlation perturbation (first-order) is¹⁰ $V = u^{-1} + (e^{-2r_1} - 1)/r_1 + (e^{-2r_2} - 1)/r_2 + e^{-2r_1} + e^{-2r_2} + \frac{5}{8}$. Since V depends on r_1, r_2 as well as $u = r_{12}$, we have to employ generalization (a). However, the resulting perturbation equations are again (18) and (19), with M defined by (20). We obtain

$$M = \left[\frac{17}{54} + \frac{17}{27} u - \frac{17}{18} u^2 + \frac{15}{8} u^3 - \frac{5}{12} u^4 \right] e^{-2u} - \left[\frac{17}{54} + \frac{34}{27} u + \frac{4}{9} u^2 \right] e^{-4u},$$

and carrying out the integrations we find that

$$f_{\text{corr}} = \frac{1}{16Z} \left\{ -5u + 15 \ln \left(u^2 + \frac{3}{2} u + \frac{3}{4} \right) - \frac{3793}{81} \sqrt{3} \arctan \left(\frac{4u + 3}{\sqrt{3}} \right) + \right.$$

$$\frac{136}{27} \frac{e^{-2u}}{u} - \frac{1}{27} + \frac{272}{27} \int_0^u \frac{x + \frac{25}{17}}{x^2 + \frac{3}{2}x + \frac{4}{3}} e^{-2x} dx \Big\} + \text{const.},$$

and¹⁶ $\bar{E}_2^{\text{corr}} = -0.032435$ Hartree. This is 70 per cent of the accurate Hartree-Pock second-order correlation energy -0.046663 Hartree. Kirtman and Benston's application to the total first-order wave function yielded only 51 per cent.

It is interesting to compare the behavior of the two approximate first-order factors for small u and large u :

$$\begin{aligned} Zf &\approx \text{const.} + \frac{1}{2}u - \frac{5}{48}u^2 + O(u^3) \\ &\sim \frac{5}{16}u + \frac{1}{8}\ln u + \text{const.} + O(u^{-1}) \\ Zf_{\text{corr}} &\approx \text{const.} + \frac{1}{2}u - \frac{217}{1296}u^2 + O(u^3) \\ &\sim -\frac{5}{16}u + \frac{15}{8}\ln u + \text{const.} + O(u^{-1}). \end{aligned}$$

We note that both satisfy the cusp condition for the exact first-order wave function factor $f = \psi_1/\psi_0$, $Z \left(\frac{\partial f}{\partial u} \right)_{u=0} = \frac{1}{2}$. The first terms in the asymptotic expansions for large u have opposite sign, however.

Discussion.—The trial wave function (21) is not the best form of its kind. It is better to start with a trial function

$$\bar{\psi} = F(r_{12})\varphi(r_1)\varphi(r_2), \quad (23)$$

and to vary both the "correlation" factor F and the orbital function φ simultaneously. A function of this form was first considered by Baber and Hasse,¹¹ whose work was extended by Green *et al.*¹² To the first order this approach is equivalent to employing a correlation wave function with the single excitations projected out;¹⁵ that is,

$$\bar{\psi}_1^{\text{corr}} = [f(r_{12}) - g(r_1) - g(r_2)]\psi_0, \quad (24)$$

where $g(r_1) = \int \phi_0^2(r_2)f(r_{12})d\tau_2$. Roothaan and Weiss¹³ have performed variational calculations for the total energy of two-electron atoms using trial wave functions of the form (23). The extrapolation of their results for various Z to $Z = \infty$ yields¹⁴ $\bar{E}_2^{\text{corr}} = -0.0440$ Hartree, or 94 per cent of the exact value. The interaction between the factor F and the orbital φ is therefore very large and beneficial, as pointed out by Rosenfeld and Konowalow.¹⁴

Summary.—In a recent paper Kirtman and Benston¹ derived a first-order trial wave function $\bar{\psi}_1$ for a perturbed Hamiltonian $H_0 + V$ of the form $\bar{\psi}_1 = f(V)\psi_0$. The object of this paper is to extend their idea to the total Schrödinger equation, and to use functional minimization to obtain the best trial wave function of the

form $\bar{\psi} = F(V)\psi_0$. The resulting equation for the first-order wave function agrees with theirs. The theory is applied to the first-order correlation problem for two electron atoms, and accounts for 70 per cent of the second-order correlation energy.

* This research was supported by National Aeronautics and Space Administration grant NSG-275-62 and by a National Science Foundation graduate fellowship.

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¹³ Roothaan, C. C. J., and A. W. Weiss, *Rev. Mod. Phys.*, **32**, 194 (1960).

¹⁴ Rosenfeld, J. L. J., and D. D. Konowalow, *J. Chem. Phys.*, **41**, 3556 (1964).

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The two appendices of this report contain further details.

COMMENT ON VAN DER AVOIRD'S WAVE OPERATOR FORMALISM

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In regard to the papers on the perturbation theory of forces by Van der Avoird [1,2], it is worthwhile to point out that if the matrix PR_0P , defined* by eqs. 5 and 14, does not have an inverse in the space P , then the proposed solution will not satisfy the original Schroedinger equation. This follows since the set of equations

$$PR_0P(E-H)PT = PR_0P$$

will not have a unique solution, and the inverse of $PR_0P(E-H)P$, expressed as an expansion in eq. 19, will not exist.

For the case when E_0 is the ground state of H_0 , the R_0 is negative definite so that PR_0P has

an inverse and there is no difficulty**. For excited states R_0 is no longer a definite operator so that the inverse of PR_0P might not exist. Although a slight change in the definition of H_0 would correct for this, convergence problems due to this difficulty may occur in the application of the theory to excited states.

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* Here the equation numbers and notation are those of ref. [1].

** Preliminary calculations on the ground states of some simple potentials have shown that the theory gives reasonable results.

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Calculation of Matrix Elements for One-Dimensional Quantum-Mechanical Problems*

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A simple method proposed by Harris *et al.* using the techniques of transformation theory for the generation of the matrix elements of one-dimensional potential functions in a discrete, orthonormal basis is shown to be equivalent to Gaussian quadratures when the basis is constructed of orthogonal polynomials. The basis $\exp(in\theta)$ on $(-\pi, \pi)$ is also discussed.

I. INTRODUCTION

A method has been proposed by Harris *et al.*¹ and employed by several authors,² for the calculation of the matrix of a one-dimensional potential function $V(x)$ in a discrete, orthonormal basis $\phi_n(x)$, $n=0, 1, \dots, N$, where the set ϕ_n is complete for $N \rightarrow \infty$. The variable x has the range (a, b) . The implementation of the method requires the existence of a single-valued function $u(x)$ on the range (a, b) , in which case their prescription for the evaluation of the matrix elements of V is

$$\begin{aligned} V_{nm} &= \int_a^b \phi_n(x) V[x(u)] \phi_m(x) dx \\ &= \sum_{j=0}^N T_{nj} T_{mj} V[x(\lambda_j)], \quad 0 \leq n, m \leq N, \quad (1) \end{aligned}$$

where the T_{nj} and λ_j are determined by

$$\int_a^b \phi_n(x) \phi_m(x) dx = \delta_{nm} = \sum_{j=0}^N T_{nj} T_{mj}, \quad (2)$$

$$\int_a^b \phi_n(x) u(x) \phi_m(x) dx = u_{nm} = \sum_{j=0}^N T_{nj} T_{mj} \lambda_j, \quad (3)$$

i.e., the orthogonal matrix $T = (T_{nm})$ diagonalizes $u = (u_{nm})$.

For the case where the u is tridiagonal, Harris *et al.* have shown that V_{nm} is exact for V , a polynomial in u of precise degree $2N - n - m + 1$ or less. For the general case where only $u_{n,n \pm i}$, $i \leq r$, is nonvanishing, it may be shown that V_{nm} is exact for V of precise degree $(2N - n - m)/r + 1$ or less. Hence, it is desirable to employ a function u whose matrix is tridiagonal.

Since the formula (1) is very suggestive of an $(N+1)$ -point mechanical quadrature, it may be compared with the Gaussian-type quadrature of the same order. In the present paper, the relationship of (1) to Gaussian quadratures is considered for: (i) the set ϕ_n constructed from orthogonal polynomials on (a, b) and; (ii) $\phi_n = (2\pi)^{-1/2} \exp(in\theta)$ on $(-\pi, \pi)$.

II. ORTHOGONAL POLYNOMIALS

If $u(x) = x$, and the basis ϕ_n is obtained from the first $N+1$ polynomials in x orthogonal with respect to

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¹ D. O. Harris, G. G. Engerholm, and W. D. Gwinn, J. Chem. Phys. 43, 1515 (1965).

² (a) D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, J. Chem. Phys. 44, 3467 (1966); (b) D. F. Zetik and F. A. Matsen, J. Mol. Spectry. 24, 122 (1967); (c) P. F. Endres, J. Chem. Phys. 47, 798 (1967); (d) C. Schwartz, J. Comput. Phys. 3, 90 (1967).

the positive weight function $w(x)$ on (a, b) , i.e., if

$$\phi_n(x) = [w(x)/h_n]^{1/2} f_n(x), \quad n=0, 1, \dots, N, \quad (4)$$

where

$$\int_a^b f_n(x) f_m(x) w(x) dx = h_n \delta_{nm}$$

and

$$f_n(x) = k_n x^n + k_n' x^{n-1} + \dots, \quad (5)$$

then the equivalence of (1) and a Gaussian quadrature may be explicitly demonstrated.

Using the Gaussian quadrature defined by $w(x)$ on (a, b) , the formula for V_{nm} is³

$$V_{nm} = \sum_{j=0}^N (h_n/h_m)^{-1/2} W_j^{(N)} f_n(a_j^{(N)}) f_m(a_j^{(N)}) V(a_j^{(N)}), \quad (6)$$

where the $a_j^{(N)}$ are the zeros of f_{N+1} ,

$$f_{N+1}(a_j^{(N)}) = 0, \quad j=0, 1, \dots, N \quad (7)$$

and

$$W_j^{(N)} = -k_{N+1} h_{N+1} / k_{N+1}' (a_j^{(N)}) f_{N+2}(a_j^{(N)}), \quad (8)$$

where $f'(x) = df/dx$. In the following the explicit dependence of the $a_j^{(N)}$ and $W_j^{(N)}$ upon N will be suppressed.

To establish the identity of (1) and (6) it is necessary to prove the following relations:

(i) $\lambda_j [\text{Eq. (3)}] = a_j [\text{Eq. (7)}]$, where both are arranged monotonically;

(ii) $T_{nj} = (W_j/h_n)^{1/2} f_n(a_j)$.

The statement (i) follows from the recursion relation⁴ among the f_n

$$f_{n+1} = (A_n + B_n x) f_n - C_n f_{n-1}, \quad (9)$$

where

$$A_n = B_n [(k_{n+1}/k_{n+1}) - (k_n'/k_n)],$$

$$B_n = k_{n+1}/k_n,$$

$$C_n = B_n h_n / B_{n-1} h_{n-1}. \quad (10)$$

This greatly simplifies the construction of the secular equation to determine the λ_j ,

$$D_{N+1}(\lambda_j) = 0, \quad j=0, 1, \dots, N, \quad (11)$$

where

$$D_N(\lambda) = (-)^N k_N \det(\alpha - \lambda I), \quad (12)$$

and α and I are of dimension $N \times N$.

Expanding along the last row of (12), we see that the D_N satisfy the recursion relation

$$D_{N+1}(\lambda) = (A_N + B_N \lambda) D_N(\lambda) - C_N D_{N-1}(\lambda). \quad (13)$$

It is easy to check that $D_1(\lambda) = f_1(\lambda)$ and $D_2(\lambda) = f_2(\lambda)$ so that by (13), $D_N(\lambda) = f_N(\lambda)$ for all $N > 0$, and hence (11) is the same as (7). This demonstrates statement (i).

To show the validity of (ii) we make use of two identities which are easily derived from Eq. (9). The first is a special case of the Christoffel-Darboux identity,⁴

$$\sum_{n=0}^N h_n^{-1} f_n(a_i) f_n(a_j) = \delta_{ij} W_j^{-1}, \quad (14)$$

and the second is

$$\sum_{n=0}^N h_n^{-1} f_n(a_i) f_n(a_j) A_n B_n^{-1} = -\delta_{ij} a_j W_j^{-1} + \sum_{n=0}^N \frac{f_{n+1}(a_i) f_n(a_j) + f_n(a_i) f_{n+1}(a_j)}{h_n B_n}, \quad (15)$$

where a_i, a_j are zeros of f_{N+1} .

Let $S_{nj} = (W_j/h_n)^{1/2} f_n(a_j)$. Then (14) implies that

$$\sum_{n=0}^N S_{nj} S_{nk} = \delta_{jk}, \quad (16)$$

and (15) implies that

$$\sum_{n=0}^N \sum_{m=0}^N S_{nj} S_{mk} x_{nm} = a_j \delta_{jk} = \lambda_j \delta_{jk}. \quad (17)$$

Hence, the S_{nj} are the elements of an orthogonal matrix which diagonalizes x . Since the eigenvalues of the latter matrix are nondegenerate,⁵ the elements S_{nj} are unique and thus equal to the T_{nj} .

Thus, since (1) is a Gaussian quadrature when the ϕ_n are obtained from (4) and (5), V_{nm} will be exact for V , a polynomial of precise degree p , where $p \leq (2N+1-n-m)$, as was shown by Harris *et al.*

For many of the basis sets satisfying (4) and (5) likely to be employed in problems of physical interest there exist corresponding quadratures with published values⁵ of the a_j , which substantially reduces the effort required to diagonalize x .

III. THE BASIS $\exp(in\theta)$

Where the basis functions ϕ_n do not satisfy (4) and (5), the transformation method may again be equivalent to a Gaussian quadrature, but not necessarily to the most efficient choice of weight function $w(x)$. The

³ A. Ralston, *A First Course in Numerical Analysis* (McGraw-Hill Book Co., New York, 1965), pp. 85-111.

⁴ G. Szegő, *Orthogonal Polynomials* (American Mathematical Society Colloquium Publications, New York, 1959), Vol. 23, Sec. 3.2.

⁵ A. H. Stroud and D. Secrest, *Gaussian Quadrature Formulas* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1966).

basis $\exp[i(n-N)\theta]$, $-\pi \leq \theta \leq \pi$, $n=0, 1, \dots, 2N$, discussed by Harris *et al.* may be taken as an example.

It is assumed that V is a polynomial of precise degree p in $u = \cos\theta$. Since u is tridiagonal in this basis, the characteristic polynomials D_N , defined by (12), satisfy a three-term recursion relation. This is easily identified as that satisfied by the Chebyshev polynomials of the second kind,⁶ $U_n(x)$. It should be noted that the zeros of U_n can be written in closed form, and T can be obtained from statement (ii) above. Therefore, by (6) the matrix transformation technique evaluates the $(2N+1)$ -point Gauss-Chebyshev quadrature (of the second kind) of the integral

$$\frac{2}{\pi} \int_0^\pi V(\cos\theta) U_n(\cos\theta) U_m(\cos\theta) \sin^2\theta d\theta, \quad 0 \leq n, m \leq 2N,$$

which is exact for $p \leq 4N+1-n-m$. On the other hand, using the relations between the U_n and the Chebyshev polynomials of the first kind T_n , V_{nm} may be written

$$V_{nm} = \frac{2}{\pi} \int_0^\pi V(\cos\theta) U_n(\cos\theta) U_m(\cos\theta) \sin^2\theta d\theta \\ + \pi^{-1} \int_0^\pi V(\cos\theta) T_{n+m+2}(\cos\theta) d\theta.$$

The second integral on the right vanishes for $p < n+m+2$ by orthogonality. The two conditions on p for V_{nm} to be exact may be combined to $p \leq 2N+1 - |2N-n-m|$, for a basis consisting of $2N+1$ functions.

The connection between the transformation method and Gaussian quadratures for this case may be clarified by applying the Wang transformation.⁷ This is equivalent to choosing as a $(2N+1)$ -term basis, the functions

$$T_n(\cos\theta), \quad 0 \leq n \leq N$$

⁶ *Handbook of Mathematical Functions*, M. Abramowitz and I. A. Stegun, Eds. (National Bureau of Standards, Washington, D.C., 1964), Chaps. 22 and 25. The D_n distinguishes between the Chebyshev polynomials of the first kind, $T_n(\cos\theta) = \cos n\theta$, and of the second kind, $U_{n-1}(\cos\theta) = (\sin n\theta)/\sin\theta$, which otherwise satisfy the same recurrence relation.

⁷ J. E. Wollrab, *Rotational Spectra and Molecular Structure* (Academic Press Inc., New York, 1967), p. 26. We are indebted to the referee for bringing this to our attention.

and

$$\sin\theta U_n(\cos\theta), \quad 0 \leq n \leq N-1.$$

These are, respectively, symmetric and antisymmetric with respect to $\theta \rightarrow -\theta$ and hence, the matrix V factors into an $(N+1) \times (N+1)$ block and an $N \times N$ block. Since the basis now consists of orthogonal polynomials, the analysis of the preceding section may be applied separately to each block. This leads to the same conditions on p for V_{nm} to be exact as given in the previous paragraph.

IV. CONCLUSIONS

The matrix transformation method provides a convenient technique for generating integrals for a one-dimensional variational problem using standard matrix manipulations. As Harris *et al.* point out, the diagonalization of u need only be performed once for a given N , if the λ_j and T are retained from problem to problem. In addition, for many cases of physical interest, a scaling parameter may be introduced into the basis, enabling several different basis sets to employ the same λ_j and T . For example, in the work of Zetik and Matsen^{2b} on the computation of vibrational-rotational energy levels, if the matrix of $u = (R-R_0)(\mu k/\hbar^2)^{-1/4}$, where the parameters have their usual significance, is computed, then the values of the independent variable R may be obtained by a suitable choice of R_0 and k .

The method does, however, add an unnecessary inflexibility to the energy eigenvalue problem in that evaluation of the matrix elements and the convergence of the eigenvalues with increasing N need not be considered simultaneously. The minimum number of values of V required for the accurate evaluation of V_{nm} is not independent of n and m and need not equal the number of basis functions required for a satisfactory representation of the wavefunction.

Note added in proof: The properties of the matrix u of Sec. II are also discussed by Wilf.⁸ See also Golub and Welsh.⁹

⁸ H. S. Wilf, *Mathematics for the Physical Sciences* (John Wiley & Sons, Inc., New York, 1962), p. 55.

⁹ G. H. Golub and J. H. Welsh, Calculation of Gauss Quadrature Rules, Computer Science Department Technical Reference CS81, Stanford University, Stanford, Calif., 1967 (unpublished).

LOCALIZED ORBITALS FOR ARBITRARY MOLECULAR WAVE FUNCTIONS *

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Localized orbitals are defined for arbitrary wave functions for atoms or molecules with even or odd numbers of electrons by making a particular non-orthogonal transformation among the natural orbitals which preserves the diagonal nature of the electron density. Different definitions of localized orbitals are obtained by relating them to different approximate forms for the wave function. The equilateral triangle configuration of H_3^+ is treated as an example.

1. INTRODUCTION

Up to now, the concept of localized orbitals [1-3] for atoms and molecules has been limited to systems described by single determinantal wave function. In the present paper we explore ways of extending this to molecules with odd or even numbers of electrons described by arbitrary wave function. The extension is not unique and is guided by relating localized orbitals to particular approximate forms for the wave function. Minimizing the energy obtained from a Hartree product of localized orbitals leads to the Edmiston-Ruedenberg criterion [2] for localization. Relating the localized orbitals to a valence bond function leads to a different criterion. These two possibilities are illustrated by considering the equilateral triangle configuration of H_3^+ .

The concept of localized orbitals was first developed extensively by Lennard-Jones, Pople, and Hall [1] for a system with high symmetry, whose wave function is a single determinant of molecular orbitals. These workers exploited the freedom to make a unitary transformation among the molecular orbitals without affecting the value of the wave function, and defined "equivalent orbitals" as linear combinations of the molecular orbitals which have the property of being identical to each other except for orientation and position in space.

Edmiston and Ruedenberg [2] and Foster and Boys [3] freed the concept of localized orbitals

from the restriction that the system be symmetric, although they still required a single determinant wave function. The technique used was to define a function of the transformation from molecular orbitals to localized orbitals, whose extreme points fix the transformation. This function provides the effective definition of "localization".

2. TRANSFORMATION TO LOCALIZED ORBITALS

We wish now to free the concept from any restriction on the form of the wave function. This we do by making use of the natural orbital expansion of the electron density $\rho(r)$:

$$\begin{aligned}\rho(r) &= \int \psi^* \sum_i \delta(r - r_i) \psi d\tau, \\ &= \sum_i \lambda_i x_i^2(r).\end{aligned}$$

The x_i and λ_i denote the i th natural orbital and its occupation number, respectively.

When ψ is a single determinant of doubly-occupied orbitals, all λ_i equal two and the form of ρ is invariant to an orthogonal transformation among the x_i . In the more general case, the form of ρ is invariant to the non-orthogonal transformation

$$n_i^{\frac{1}{2}} u_i = \sum_j T_{ij} \lambda_j^{\frac{1}{2}} x_j,$$

where T is unitary and n_i normalizes u_i . Then

$$\rho(r) = \sum_i n_i u_i^2(r).$$

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An essential feature of the scheme we are considering is the preservation of the form of ρ as a "sum of squares" without any cross terms. The reason for this will become apparent in the example discussed below.

The transformation T is thus far unspecified. We choose T by a straightforward generalization of the Edmiston-Ruedenberg criterion [2] for the single determinant case. Let V_{ij} be the electrostatic interaction energy of the charge distributions $n_i u_i^2$ and $n_j u_j^2$.

$$V_{ij} = n_i n_j \int \frac{u_i^2(r) u_j^2(r')}{|r - r'|} dr dr'.$$

The total self-energy of ρ is invariant to T , but is equal to the sum of two terms, neither of which is invariant.

$$\frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' = \frac{1}{2} \sum_i V_{ii} + \sum_{i < j} V_{ij}.$$

(invariant) (maximize) (minimize)

We choose T to minimize the interaction sum or, equivalently, to maximize the self-energy sum.

The significance of this criterion may be seen by relating the localized orbitals u_i to an approximate wave function constructed from them. In particular, for a system of $2N$ electrons, a Hartree (rather than a Hartree-Fock)-like wave function may be constructed by doubly-occupying the first N natural orbitals. It may be shown that minimizing the energy of this wave function is equivalent to the Edmiston-Ruedenberg criterion for this case.

This suggests that another way to obtain localized orbitals is to relate them to a more accurate form for the wave function, such as a valence-bond function, or at least one which satisfies the Pauli principle. We shall explore this possibility by means of the following example.

3. EXAMPLE: H_3^+ (equilateral triangle)

We wish to consider the electron distribution of H_3^+ in the *equilateral triangle* ($R = 1.6575$ Bohr) configuration. The natural orbitals have recently been given by Christoffersen and Shull [4], based on Christoffersen's twelve configuration wave function [5]. Truncating the natural orbital expansion after three terms, we can write the wave function as

$$\psi(1, 2) = \lambda_1^{\frac{1}{2}} \chi_1(1) \chi_1(2) - \lambda_2^{\frac{1}{2}} [\chi_2(1) \chi_2(2) + \chi_3(1) \chi_3(2)],$$

where the representation of the χ_i in terms of Slater orbitals is given in ref. [4] where $\lambda_1 =$

$= 0.993594$ and $\lambda_2 = 0.079906$. The χ_1 belongs to the totally symmetric representation a_1' of D_{3h} , whereas χ_2 and χ_3 belong to the doubly-degenerate representation e' .

3.1. Localized orbitals for H_3^+

Now we can transform to three localized orbitals u_a, u_b, u_c by making use of the high symmetry. Since the natural orbitals form a basis for an irreducible representation of D_{3h} , the localized orbitals form a basis for a reducible representation. If C_3^+ denotes a counterclockwise rotation of 120° about the vertical axis, and σ_a denotes reflection through the vertical plane containing nucleus a , then a reasonable choice for the symmetry properties of u_a, u_b, u_c is

$$u_b = C_3^+ u_a; \quad u_c = C_3^+ u_b; \quad \sigma_a u_a = u_a.$$

The T is the similarity transformation which connects the representation spanned by χ_1, χ_2, χ_3 with that spanned by u_a, u_b, u_c . Because of the degeneracy of e' , group theory does not completely fix T , but rather gives two possible sets of localized orbitals, which may be generated from:

$$u_a^\pm = \lambda_1^{\frac{1}{2}} \chi_1 \pm (\lambda_1/2)^{\frac{1}{2}} (\sqrt{3} \chi_2 - \chi_3) \quad (1)$$

by application of C_3^+ . The plus sign corresponds to an atomic density polarized to a large extent toward the other atoms. The minus sign corresponds to a bond density polarized toward the non-bonded atom. The orbital which is the more localized, i.e. which maximizes

$$V_{aa} = \int u_a(r) u_a(r') |r - r'|^{-1} dr dr'$$

is u_a^+ . Its representation in terms of Slater orbitals is given in table 1.

3.2. Valence bond form

The preceding analysis characterizes the total density as a sum of three localized densities. A different sort of analysis is suggested by relating the natural orbital expansion of the *wave function* to a valence bond form, namely,

$$\psi(1, 2) = M[\phi_{ab} + \phi_{bc} + \phi_{ac}],$$

where

$$\begin{aligned} \phi_{ab} &= a(1)b(2) + b(1)a(2), \\ (\lambda_1^{\frac{1}{2}} + 4\lambda_2^{\frac{1}{2}})^{\frac{1}{2}} a &= \lambda_1^{\frac{1}{2}} \chi_1 + \lambda_2^{\frac{1}{2}} (\sqrt{3} \chi_2 - \chi_3). \end{aligned} \quad (2)$$

We have simply rearranged the three term natural orbital expansion of the wave function to have this form, and have required a, b and c to have the same symmetry properties as previously assigned to u_a, u_b, u_c . The orbital a is an atomic

Table 1
Expansions of the orbitals ψ_a , a , a_{ab} in terms of Slater orbitals for H_3^+ (equilateral triangle)

| | Slater orbitals | ψ_a^+ (eq. 1) | a (eq. 2) | a_{ab} (eq. 3) |
|----|---|-----------------------|----------------|---------------------|
| 1s | $(\zeta_1^3/\eta)^{1/2} \exp(-\zeta_1 r_a)$ | +0.638 | +1.169 | +0.932 |
| | $(\zeta_1^3/\eta)^{1/2} \exp(-\zeta_1 r_b)$ | +0.376 | +0.023 | -0.067 |
| | $(\zeta_1^3/\eta)^{1/2} \exp(-\zeta_1 r_c)$ | +0.376 | +0.023 | +0.433 |
| 2s | $(\zeta_2^5/\eta)^{1/2} r_a \exp(-\zeta_2 r_a)$ | -0.116 | -0.164 | -0.142 |
| | $(\zeta_2^5/\eta)^{1/2} r_b \exp(-\zeta_2 r_b)$ | -0.088 | -0.046 | -0.040 |
| | $(\zeta_2^5/\eta)^{1/2} r_c \exp(-\zeta_2 r_c)$ | -0.088 | -0.046 | -0.091 |
| 2p | $(\zeta_3^5/\eta)^{1/2} z_a \exp(-\zeta_3 r_a)$ | +0.067 | +0.140 | 0.107 |
| | $(\zeta_3^5/\eta)^{1/2} z_b \exp(-\zeta_3 r_b)$ | +0.032 | -0.012 | -0.025 |
| | $(\zeta_3^5/\eta)^{1/2} z_c \exp(-\zeta_3 r_c)$ | +0.032 | -0.012 | 0.041 |

$\zeta_1 = 1.20$, $\zeta_2 = 1.175$, $\zeta_3 = 1.80$. The p orbitals are directed from each nucleus to the center of the triangle. Thus z_a is directed from nucleus a to the center of the triangle.

orbital polarized to a slight extent toward the other nuclei. Its representation in terms of Slater orbitals is given in table 1.

3.3. Christoffersen and Shull

Christoffersen and Shull [4] have also written the wave function in a valence bond form. However, they took the orbital a in ϕ_{ab} to be different from a in ϕ_{ac} . They wrote

$$\psi(1, 2) = N[\phi_{ab} + \phi_{bc} + \phi_{ac}],$$

where

$$\begin{aligned} \phi_{ab} &= a_{ab}(1)b_{ab}(2) + b_{ab}(1)a_{ab}(2), \\ (\lambda_1^{1/2} + 2\lambda_2^{1/2})a_{ab} &= \lambda_1^{1/2}\chi_1 + (\lambda_2^{1/2}/\sqrt{2})(\chi_2 - \sqrt{3}\chi_3). \end{aligned} \quad (3)$$

The representation of a_{ab} in terms of Slater orbitals is given in table 1. Their result was a very delocalized description. The total wave function is the same as ours, however, and we see no advantage to allowing this added flexibility. It does point up an unattractive feature of this ap-

proach, namely, although the individual terms ϕ_{ab} and ϕ_{ab} are quite different, the total density given by the two functional forms is the same, due to important contributions from "overlap densities". Preserving the form of ρ as we have done in defining localized orbitals avoids this difficulty.

3.4. Comparison

Finally, let us compare the three orbitals ψ_a , a , and a_{ab} by giving their expansion in terms of Slater orbitals centered on the three nuclei. It is clear that a is the most localized having almost no contribution from the orbitals of the other nuclei, although the meaning attached to this is different from that attached to ψ_a^+ .

Thus we see that by relating the localized orbitals to different functional forms for approximate wave functions, we can arrive at different definitions for the localized orbitals. The interpretation given the localized orbitals then follows from the form of the wave function.

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